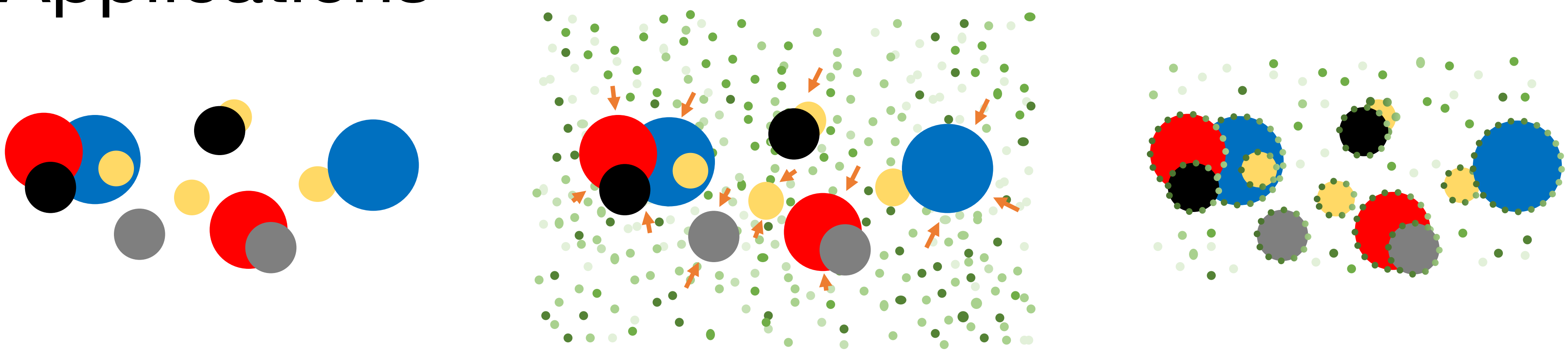
The Impact of Organic Aerosol Volatility on Aerosol Microphysics for Global Climate Modeling Applications

The science

The chemistry part

The microphysics part

I developed the model

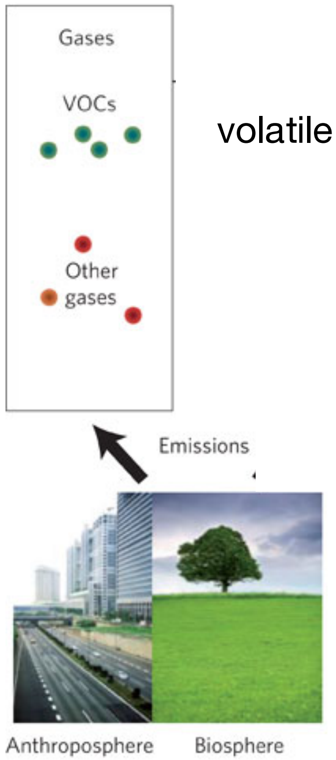


Chloe Gao

GISS Lunch Seminar

February 1, 2017

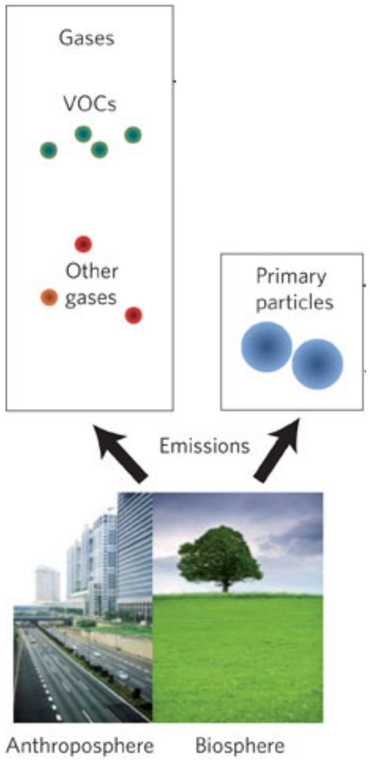
The anthroposphere and biosphere emit gases



volatile organic compounds

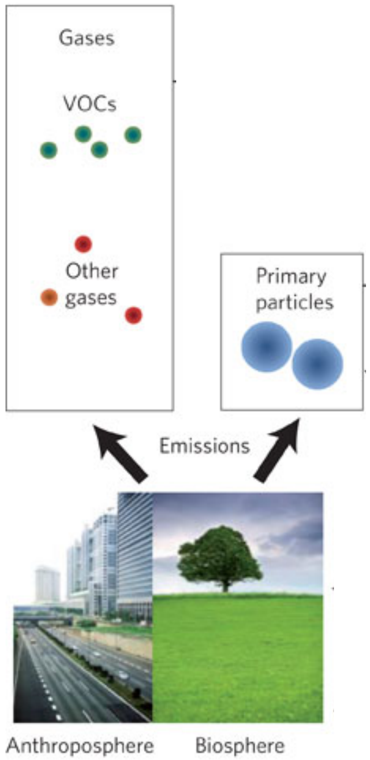
Modified Figure 1, Riipinen *et al.* 2012

The anthroposphere and biosphere also emit particles



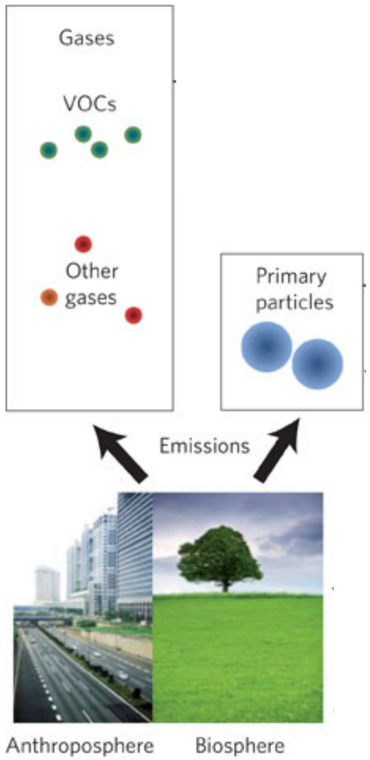
Modified Figure 1, Riipinen *et al.* 2012

Aerosols are liquid or solid particles suspended in air



Modified Figure 1, Riipinen *et al.* 2012

Aerosols have various sources and compositions



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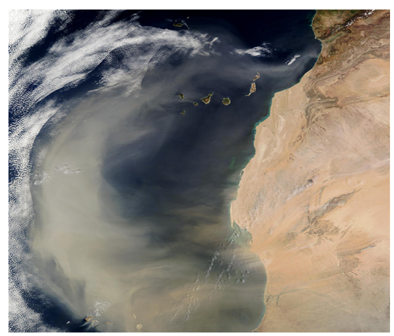
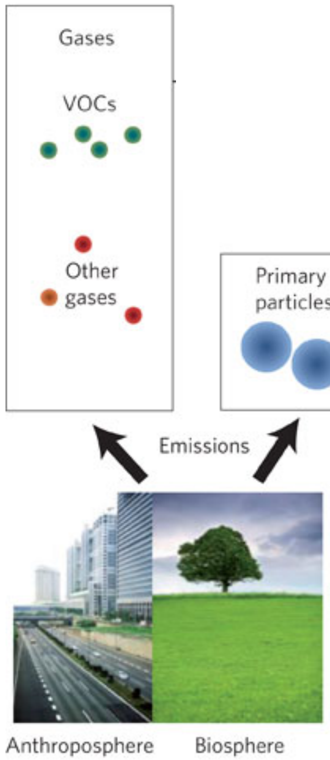
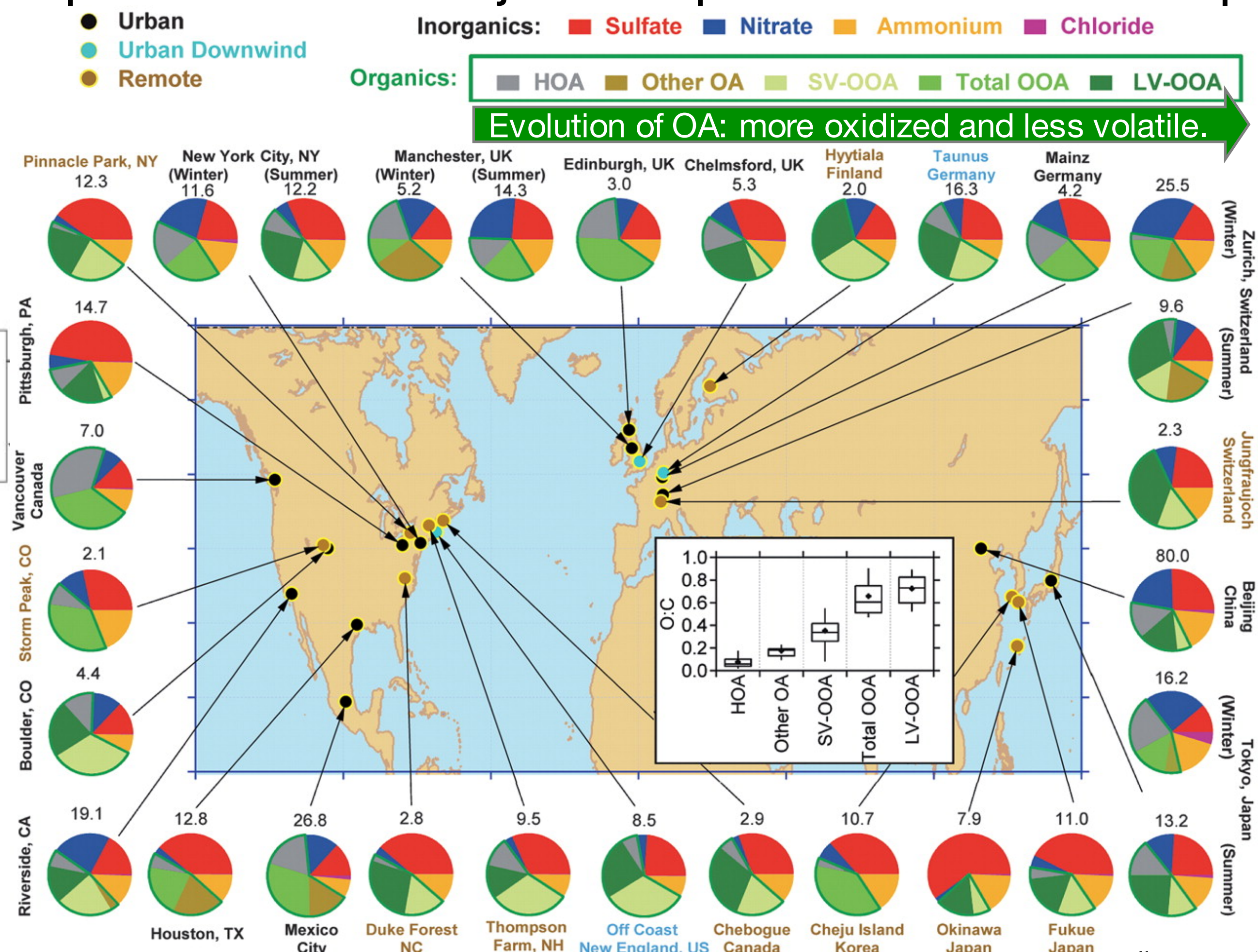


Organic aerosols are ubiquitous and a major component of the atmosphere

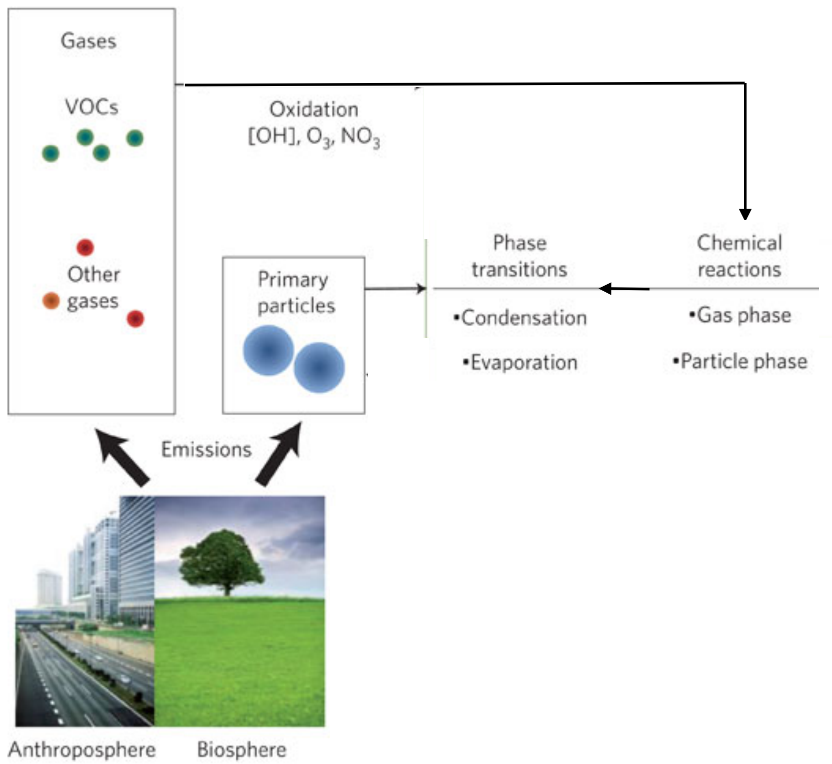


Modified Figure 1, Riipinen *et al.* 2012



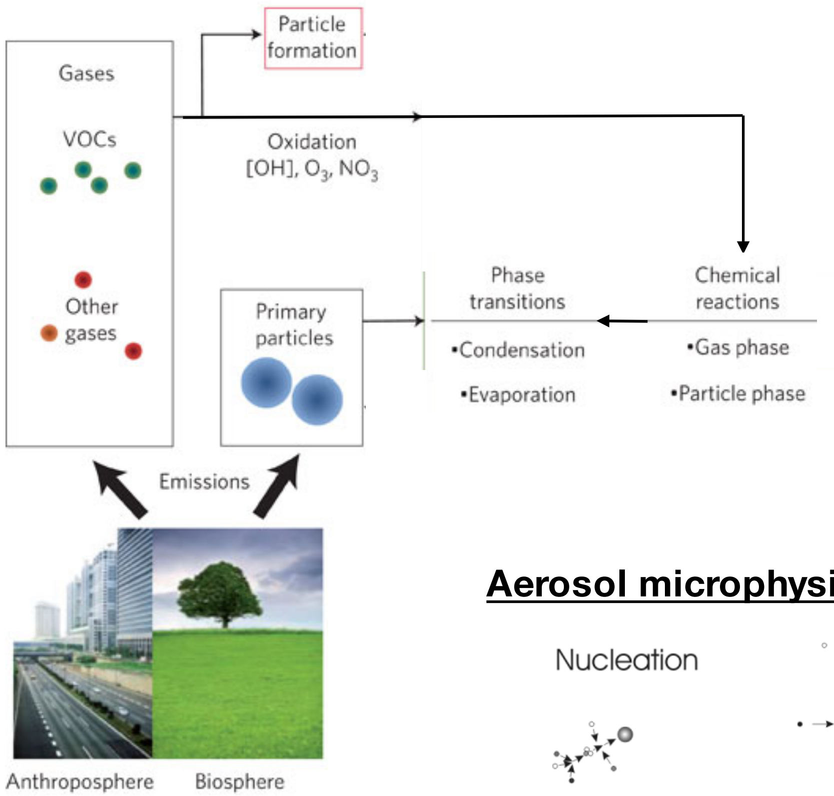
Jimenez *et al.* 2009

Organic aerosols become more oxidized and less volatile with age



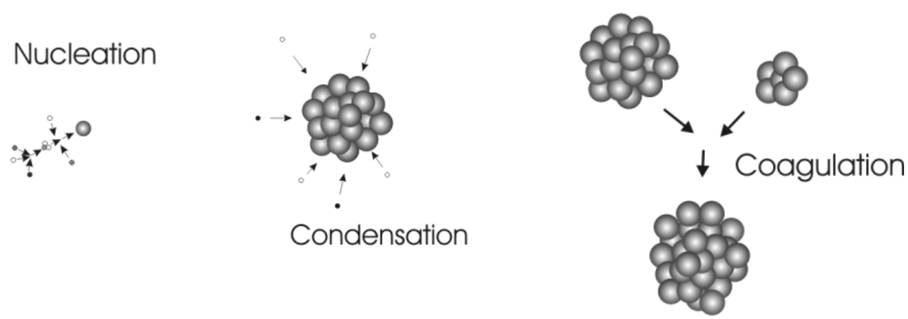
Modified Figure 1, Riipinen *et al.* 2012

The formation and growth of aerosols is considered aerosol microphysics

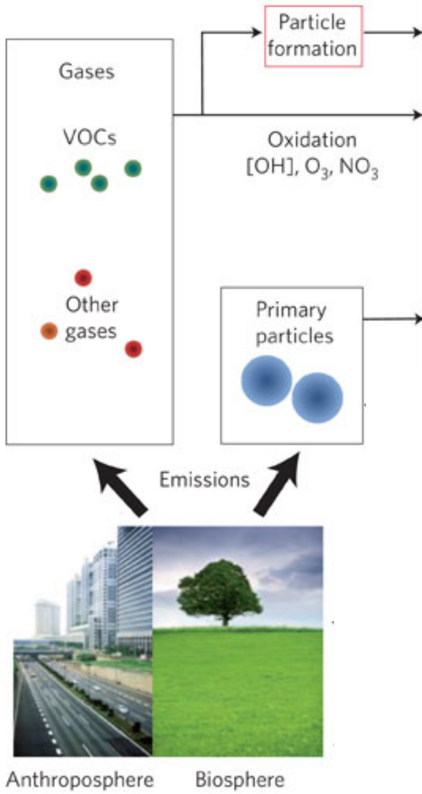


Modified Figure 1, Riipinen *et al.* 2012

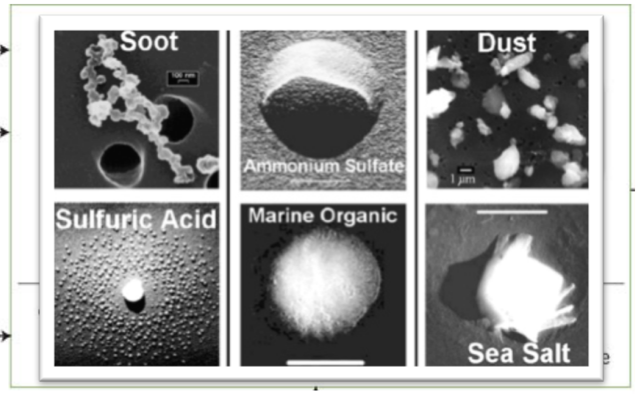
Aerosol microphysics:



Aerosols take different shapes and sizes

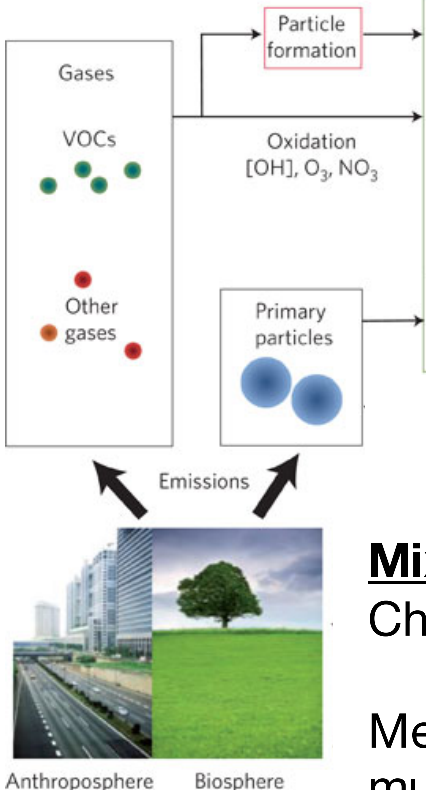


Modified Figure 1, Riipinen *et al.* 2012

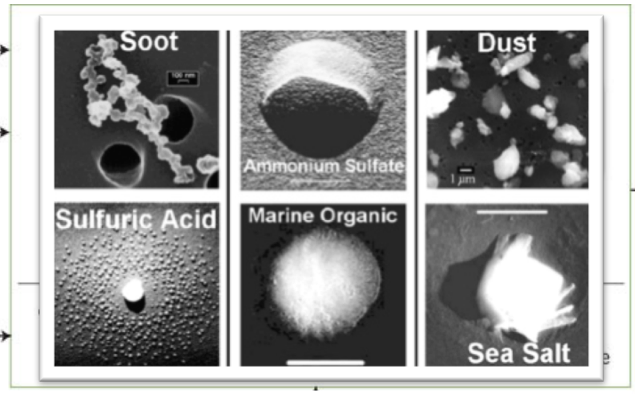


Under the microscope

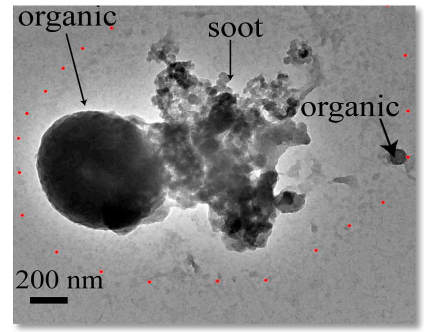
Aerosols are usually mixed, we describe them using mixing state



Modified Figure 1, Riipinen *et al.* 2012



Under the microscope



But more commonly

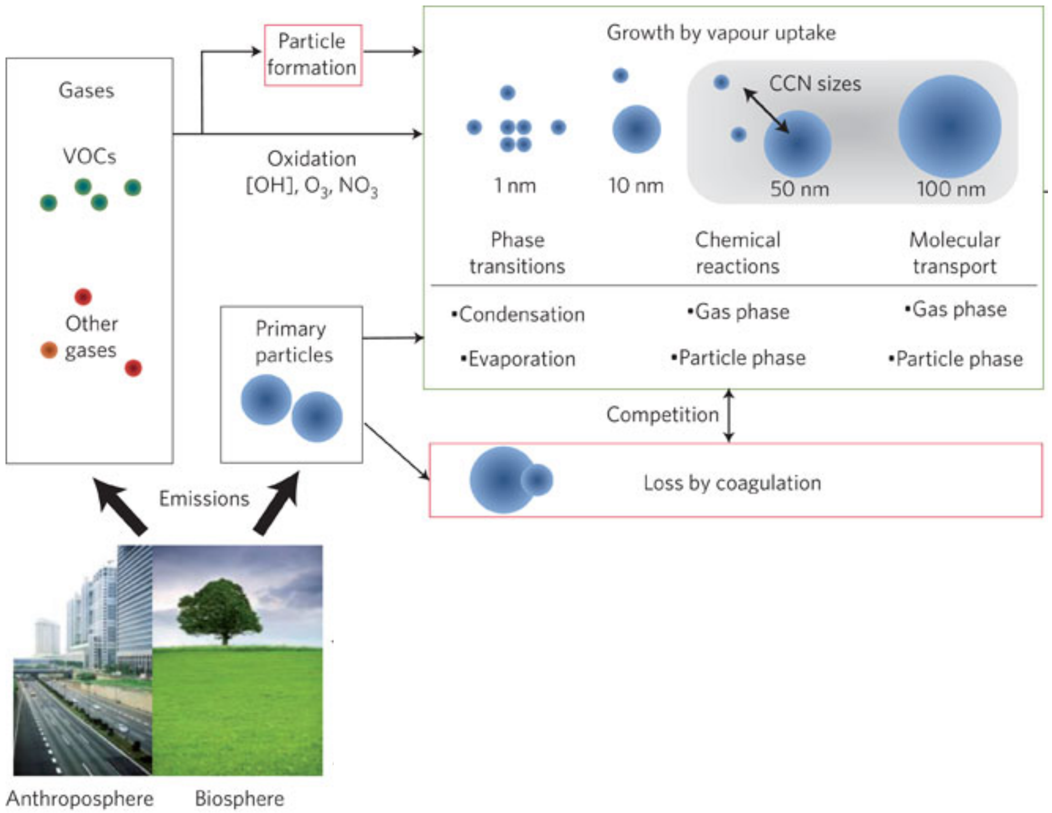
Weijun Li and Longyi Shao, JGR 2010; TEM image

<u>Mixing state:</u>

Chemical composition of single aerosol particles (real world).

Mean conditions of aerosol populations(model/obs.): How much of each chemical specie is present in a representative aerosol mix.

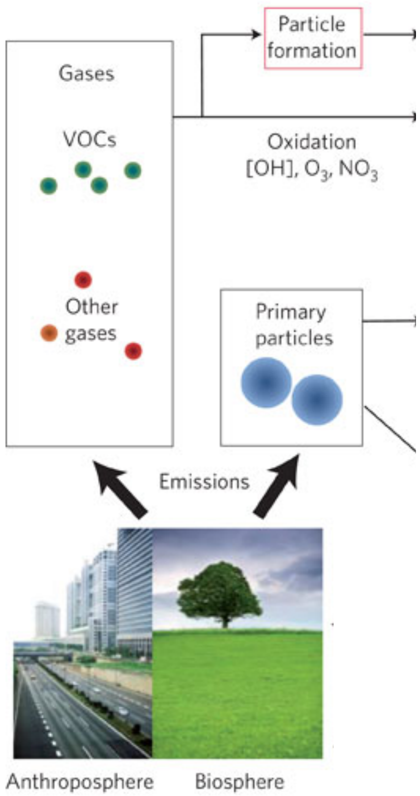
When aerosols grow, they increase in size (obviously!)



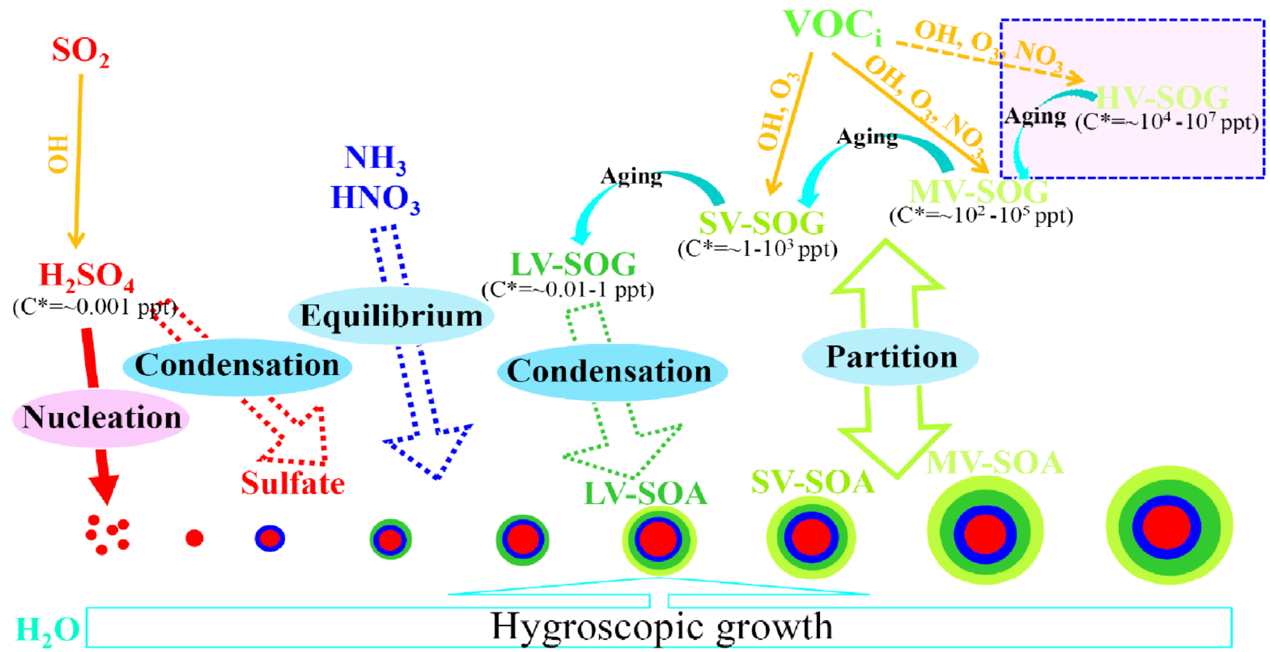
Modified Figure 1, Riipinen *et al.* 2012

The chemistry and the microphysics meet here:

the larger the aerosol, the more volatility range of gases it could take



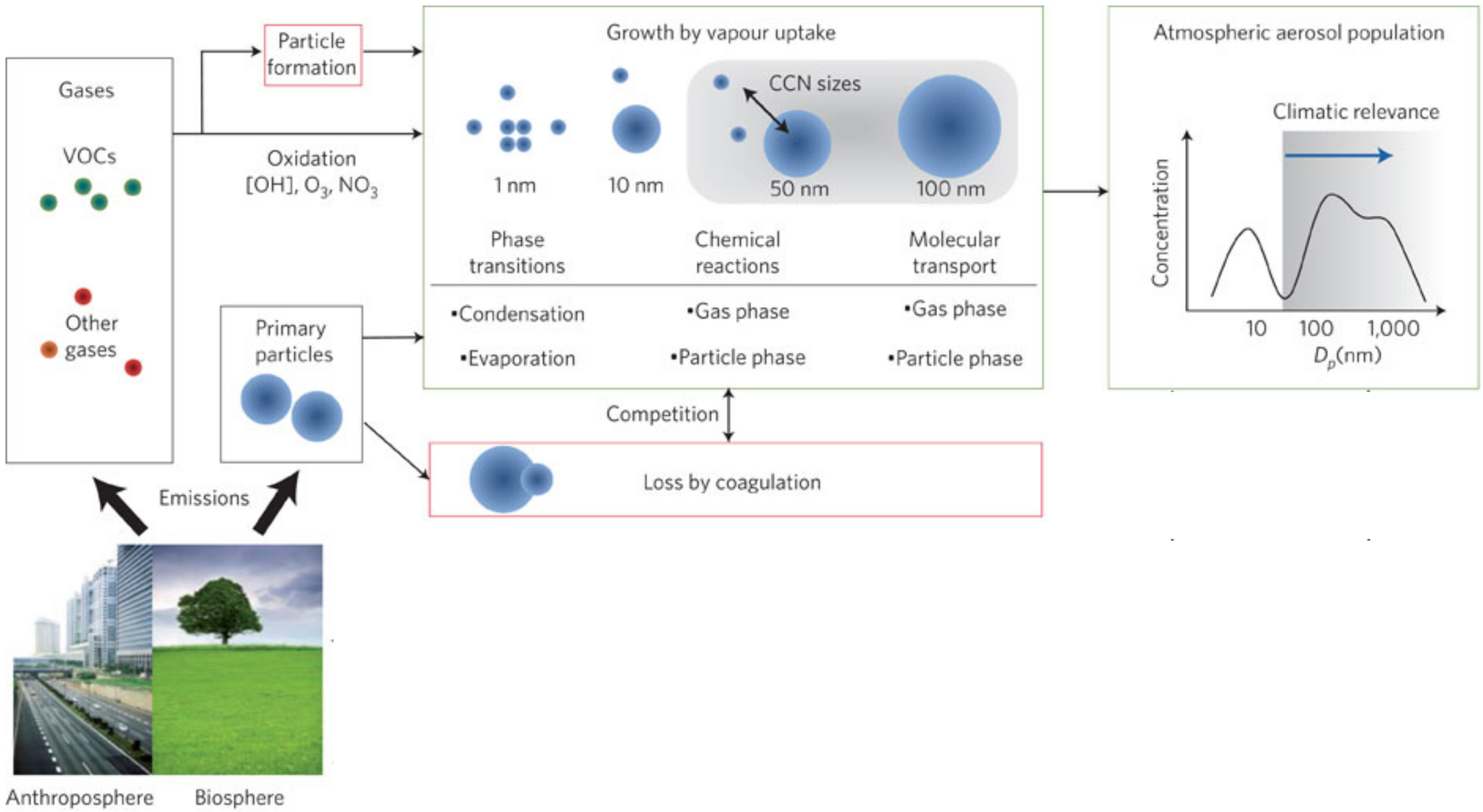
Modified Figure 1, Riipinen *et al.* 2012



Yu, 2011

Key player in particle growth!

As aerosols grow and reach certain sizes, they become climate relevant



Modified Figure 1, Riipinen *et al.* 2012

Aerosols will affect climate and air quality

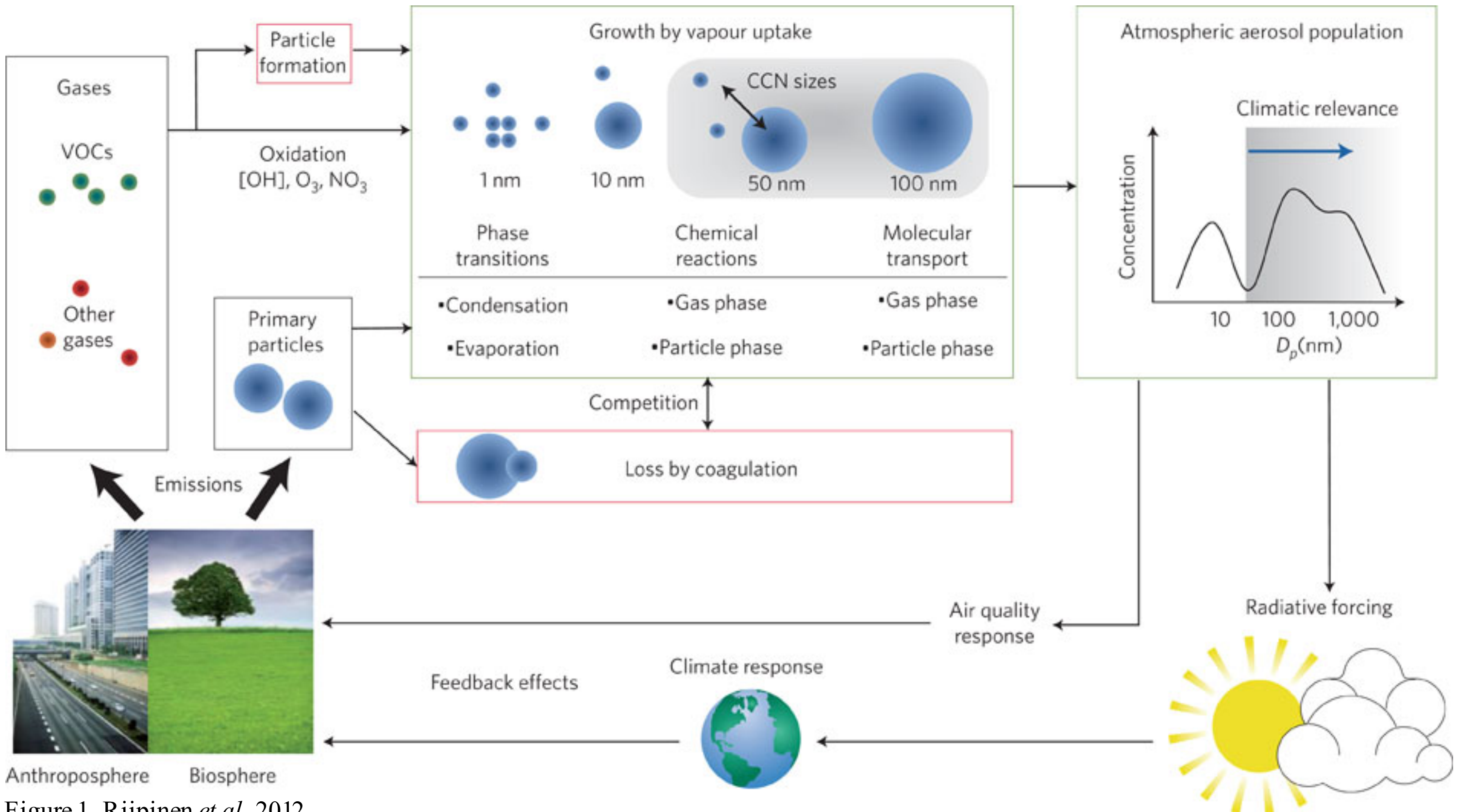
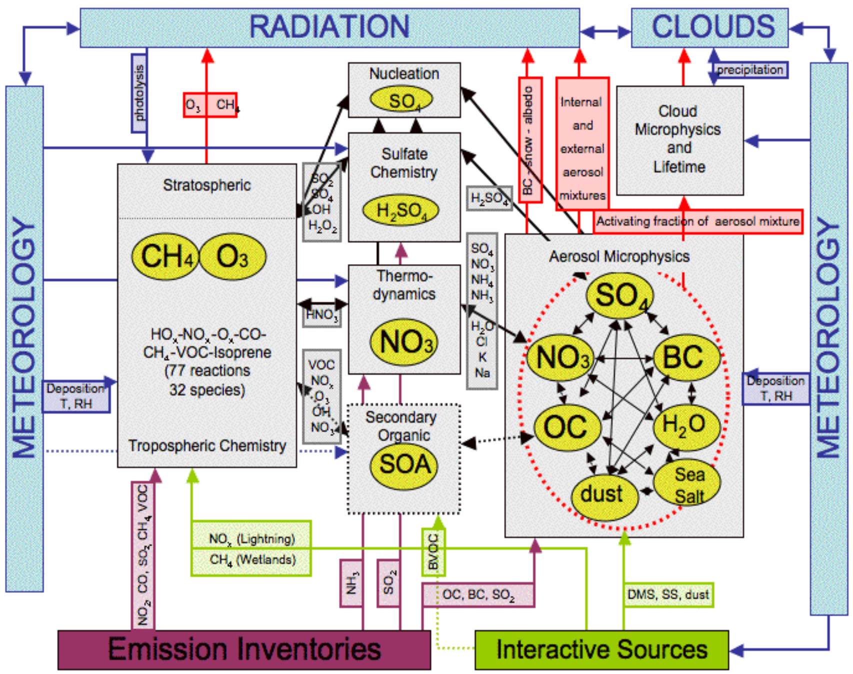


Figure 1, Riipinen *et al.* 2012

Earth Systems Models are used to simulate what's happening on our planet

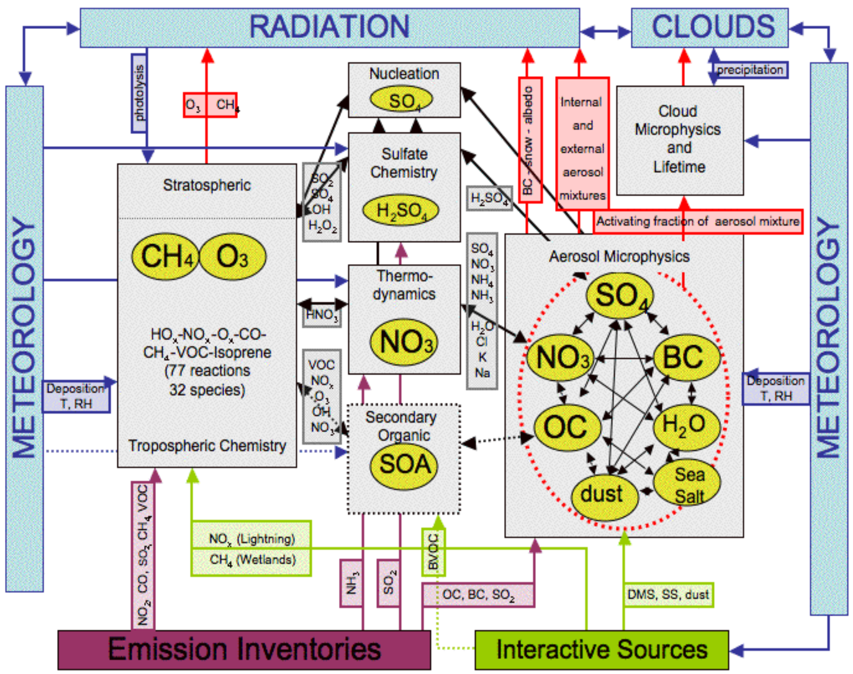
GISS modelE Earth Systems Model
(The atmosphere part)



S.E.Bauer

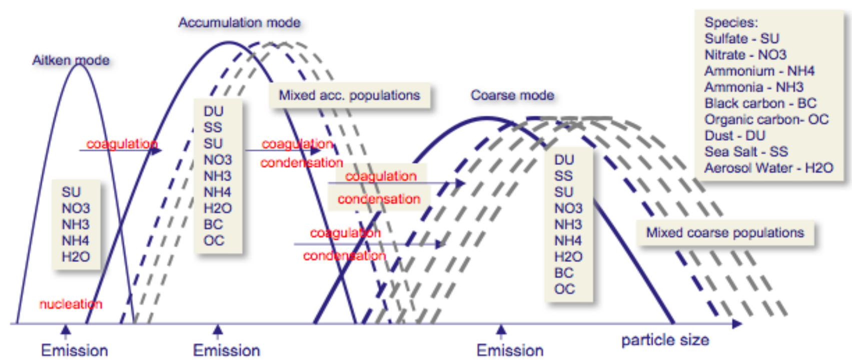
MATRIX is a aerosol microphysical model used in GISS ModelE
(Can also be used in other models… more on that later)

GISS modelE Earth Systems Model
(The atmosphere part)

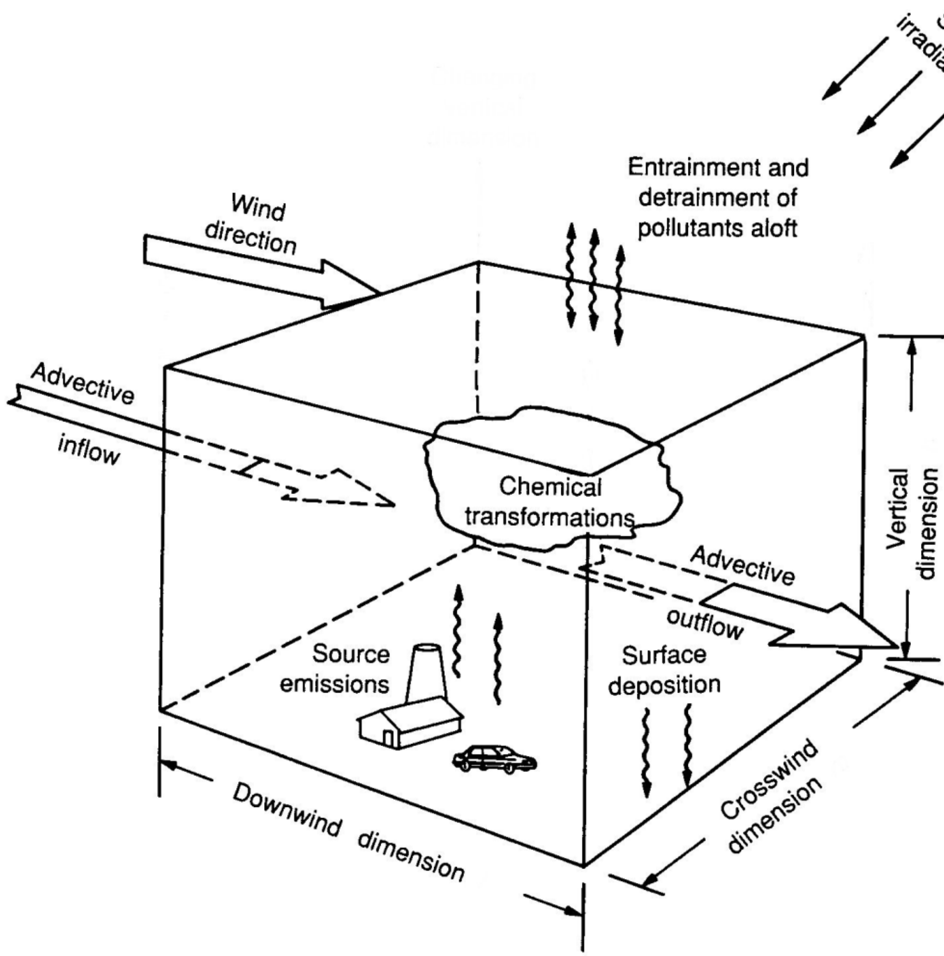


S.E.Bauer

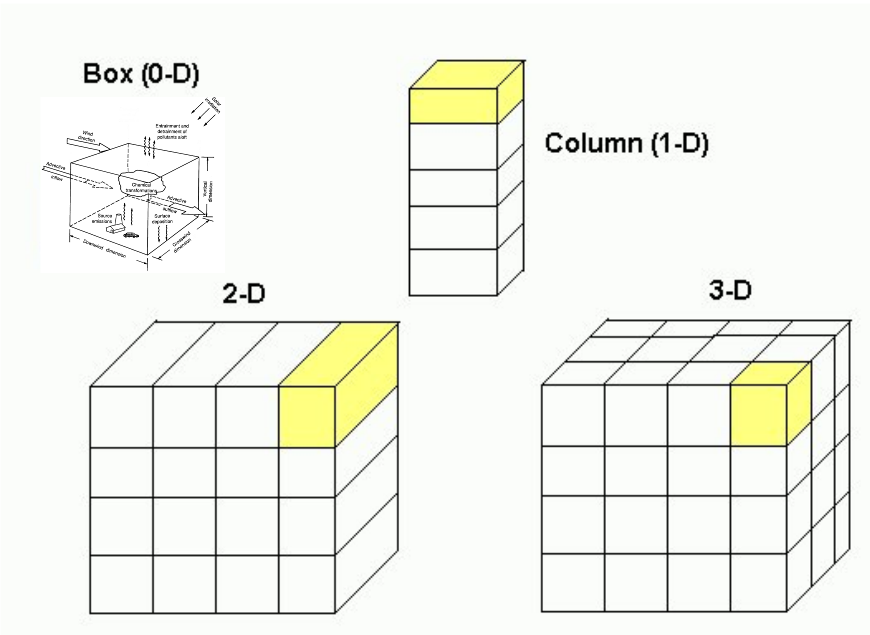
MATRIX
Aerosol Microphysical Model based on the Methods of Moments
Bauer et al. ACP 2008

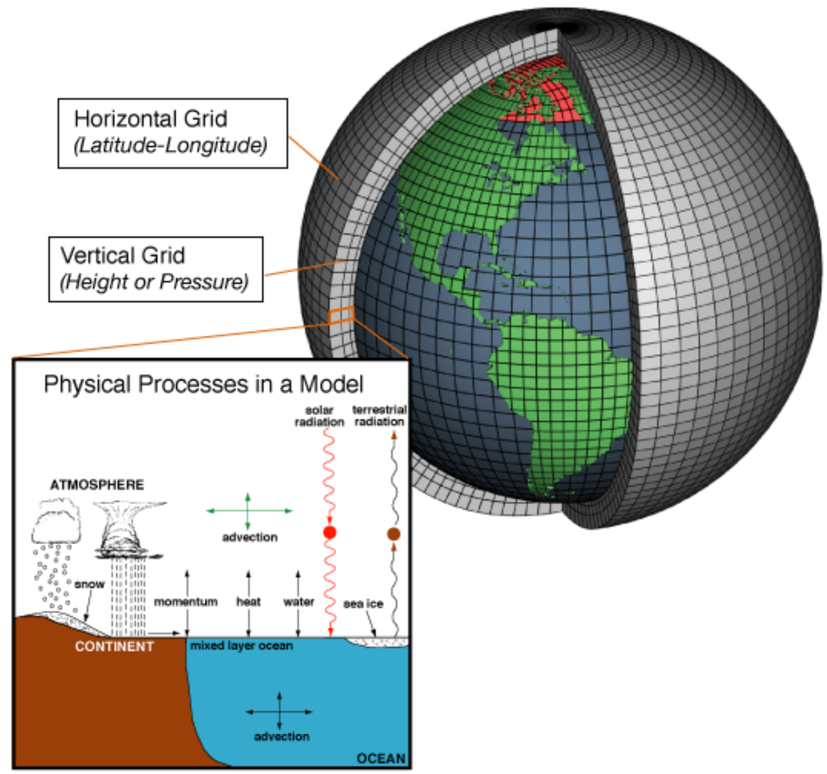


MATRIX can also be a stand-alone box model

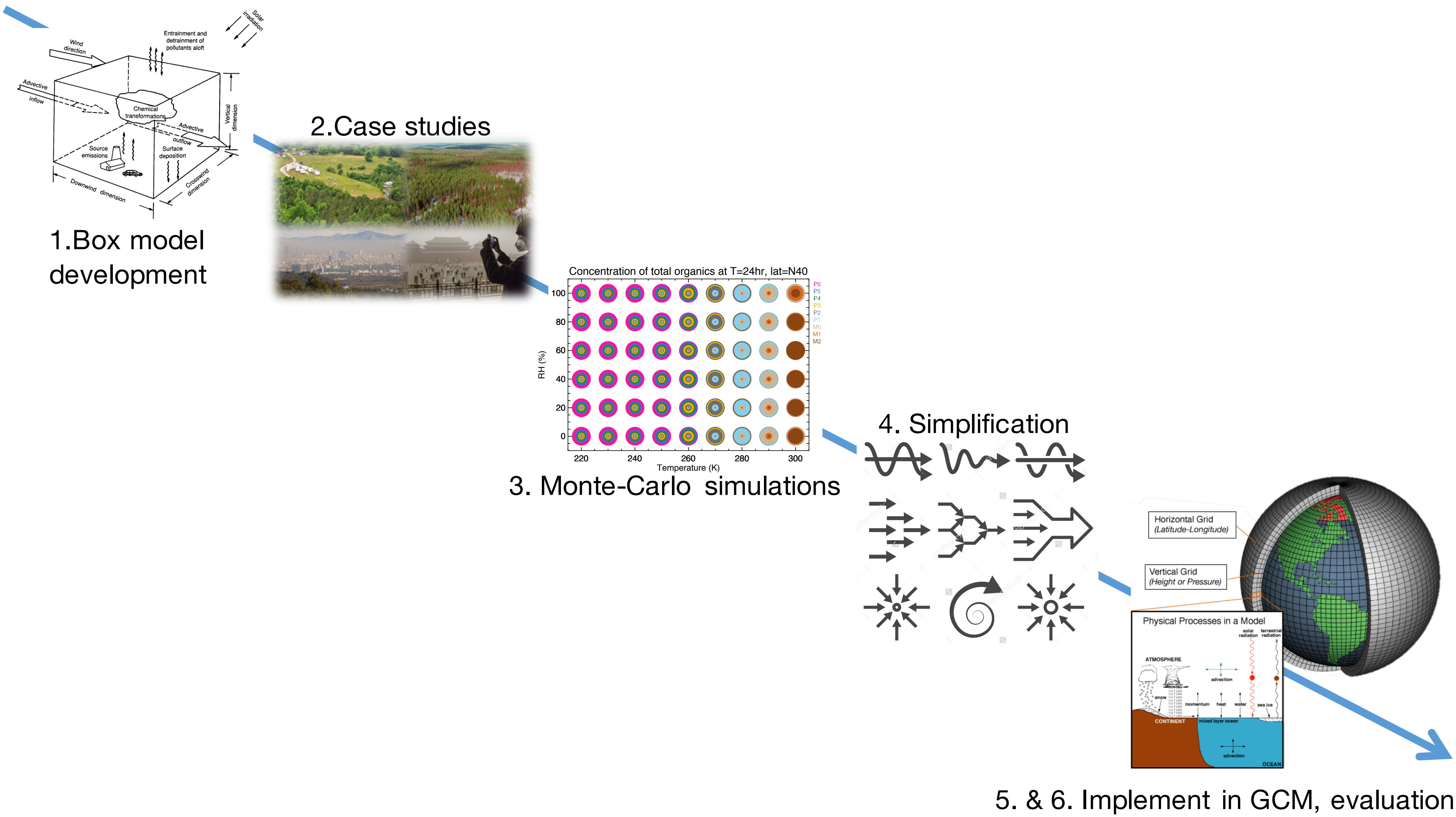


MATRIX can be a stand-alone box model or a module within a GCM





For simplicity, the model is developed as a box model, then implemented in the global model.



Solar irradiation
Entrainment and detrainment of pollutants aloft
Wind direction
Advective inflow
Chemical transformations
Advective outflow
Vertical dimension
Source emissions
Surface deposition
Downwind dimension
Crosswind dimension
1.Box model development
2.Case studies
Concentration of total organics at T=24hr, lat=N40
RH (%)
Temperature (K)
P6
P5
P4
P3
P2
P1
M0
M1
M2
3. Monte-Carlo simulations
4. Simplification
Horizontal Grid (Latitude-Longitude)
Vertical Grid (Height or Pressure)
Physical Processes in a Model
ATMOSPHERE
CONTINENT
OCEAN
5. & 6. Implement in GCM, evaluation

MATRIX scheme is coupled with the VBS framework in a box model

MATRIX (Multiconfiguration Aerosol Tracker of mIXing state)

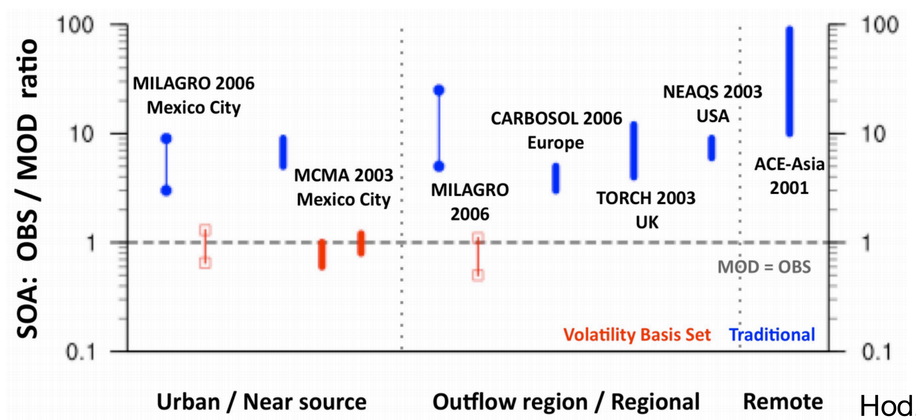
- Describes the mixing state of different aerosol populations. [*Bauer et al.* 2008]
- Organics: traditional non-volatile

+

VBS (volatility-basis set)

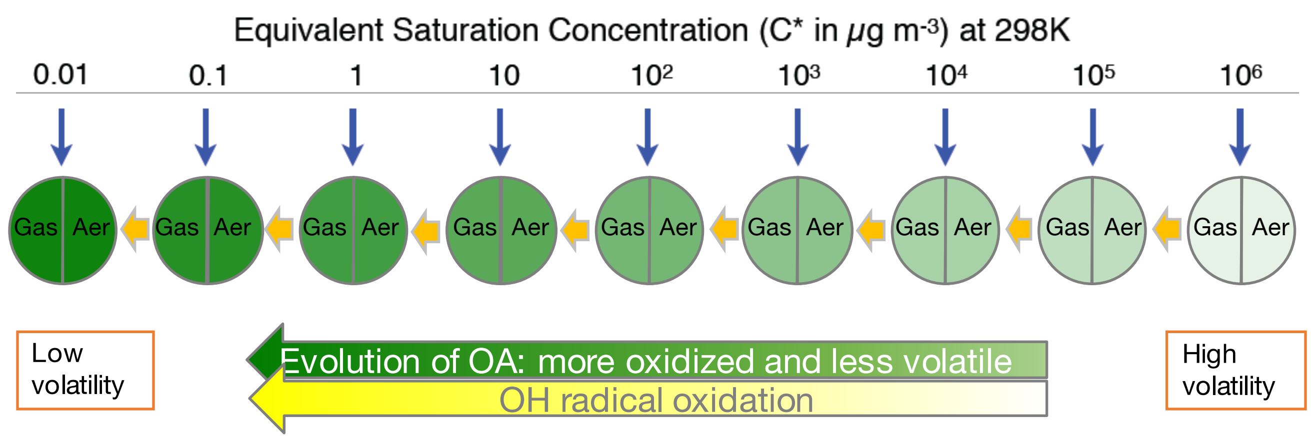
- Describes the partitioning of organic aerosols by distributing them based on their volatility into bins of effective saturation concentration. [*Donahue et al.* 2006]

✓ **MATRIX-VBS:** Organics are semi-volatile, affect size distribution by condensation & evaporation (partitioning)

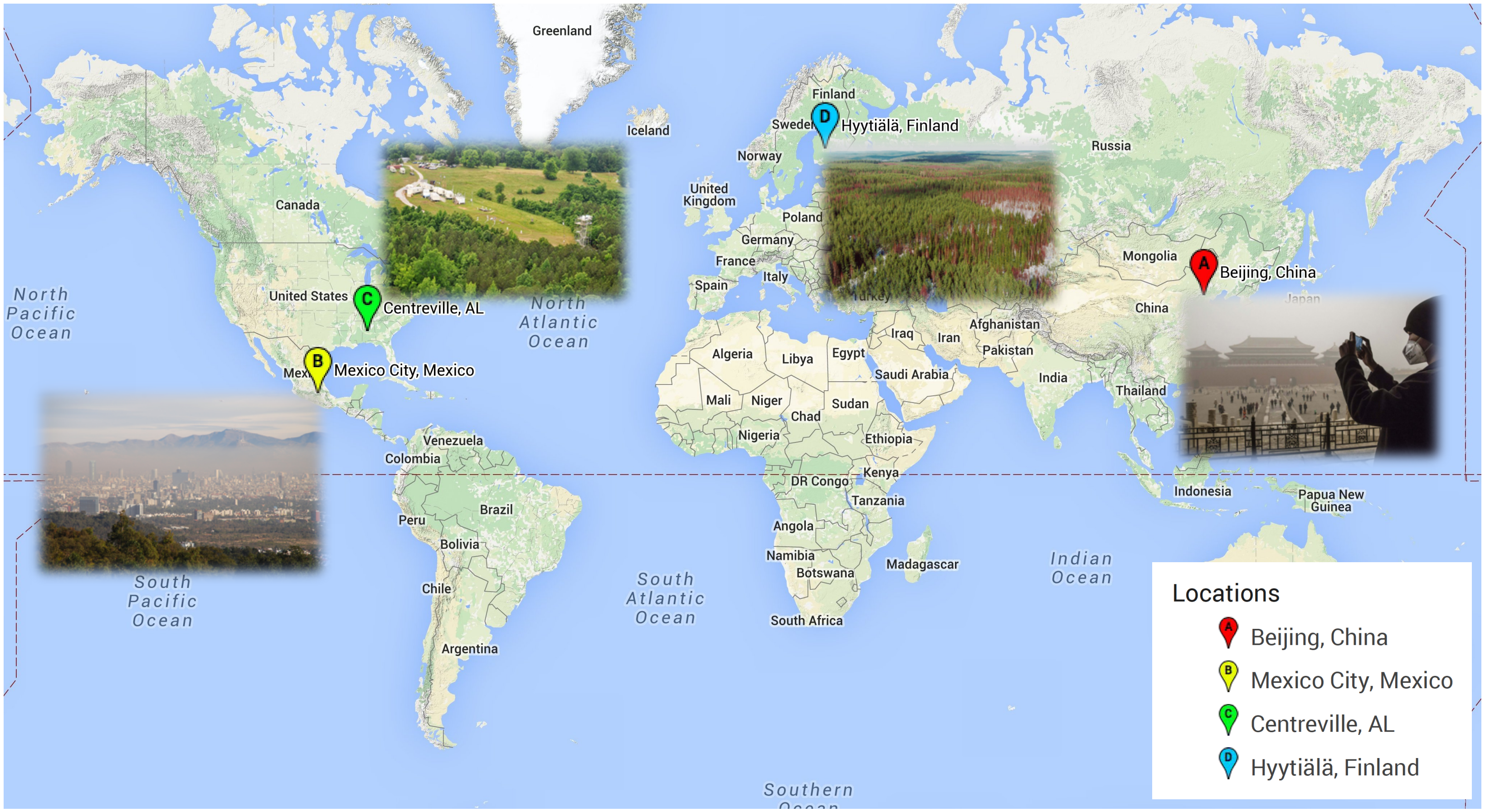


Hodzic et al., 2010

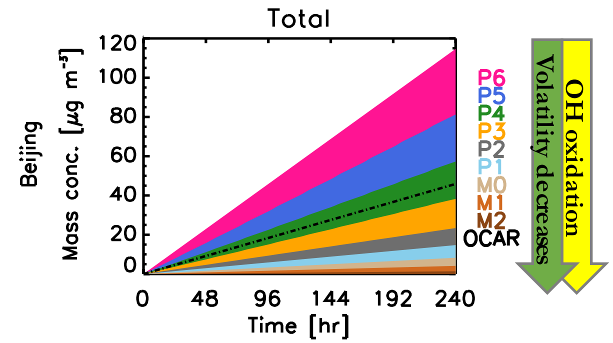
VBS separates organics by their volatility

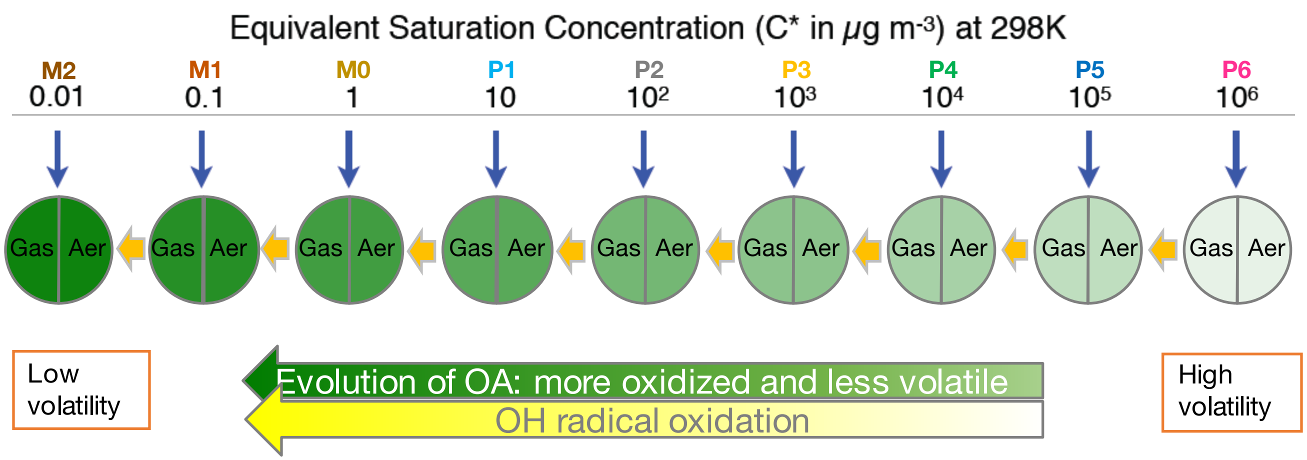


Test cases were simulated in 4 different environments for 10 days in January and July, with inputs from global model surface value outputs.



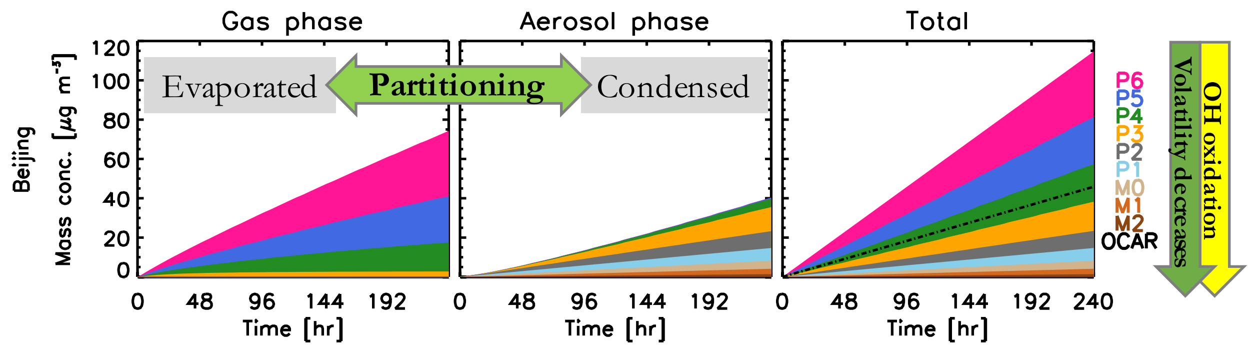
January

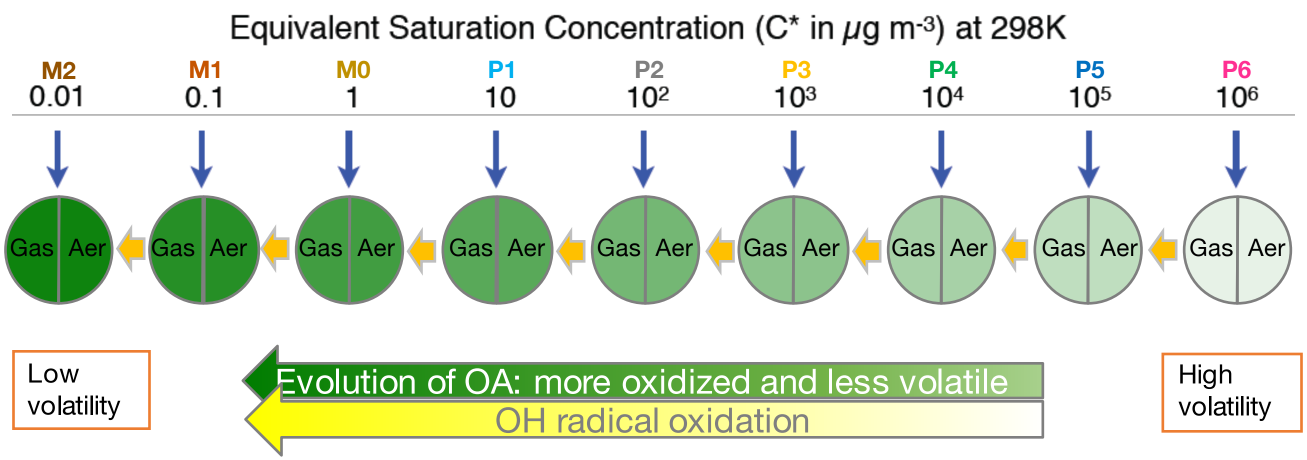




- New scheme's organics are separated into 9 bins of volatilities
- OH oxidizes high volatility organics into lower volatility organics
- New scheme's total organics 2.5x the original scheme (dashed line)

January



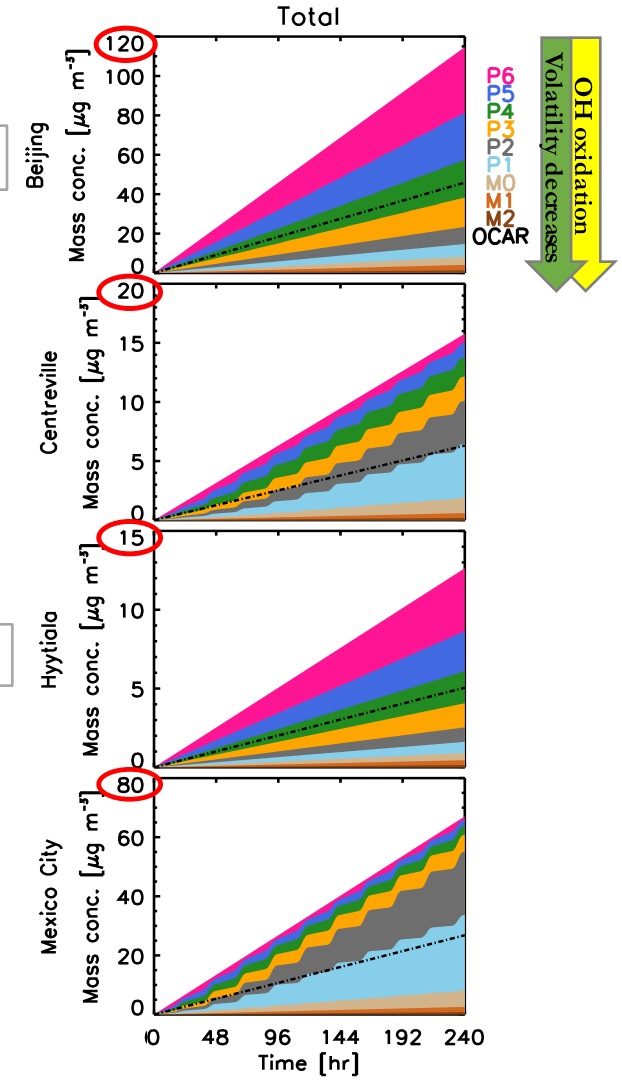


- High volatile species in the gas phase
- Low volatile species in the aerosol phase
- Intermediate volatility bins partition between gas and aerosol phase

January

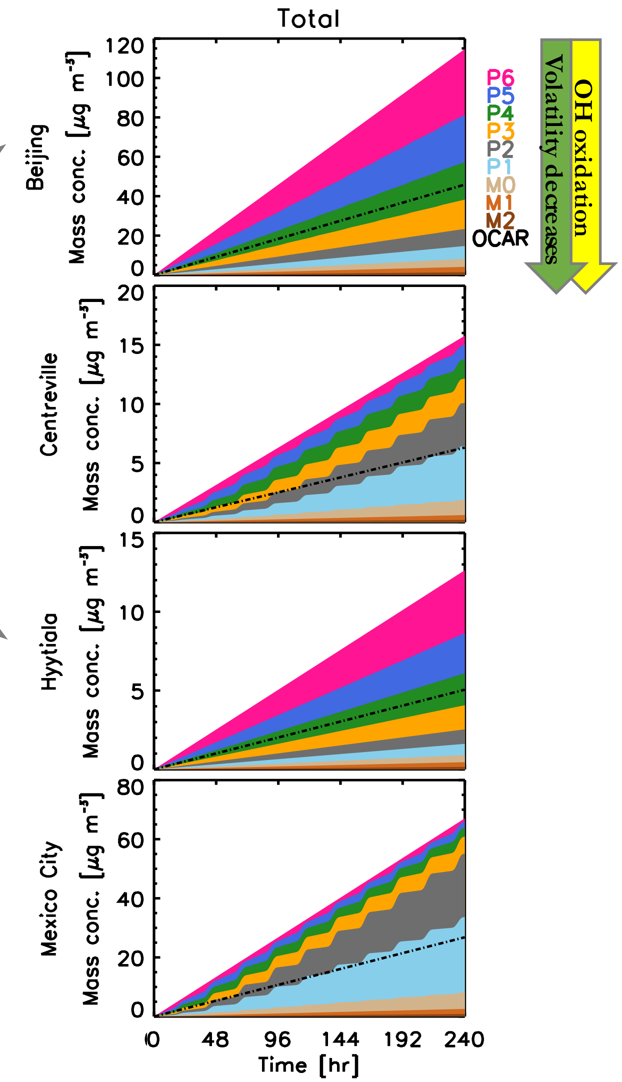
Most polluted

Least polluted



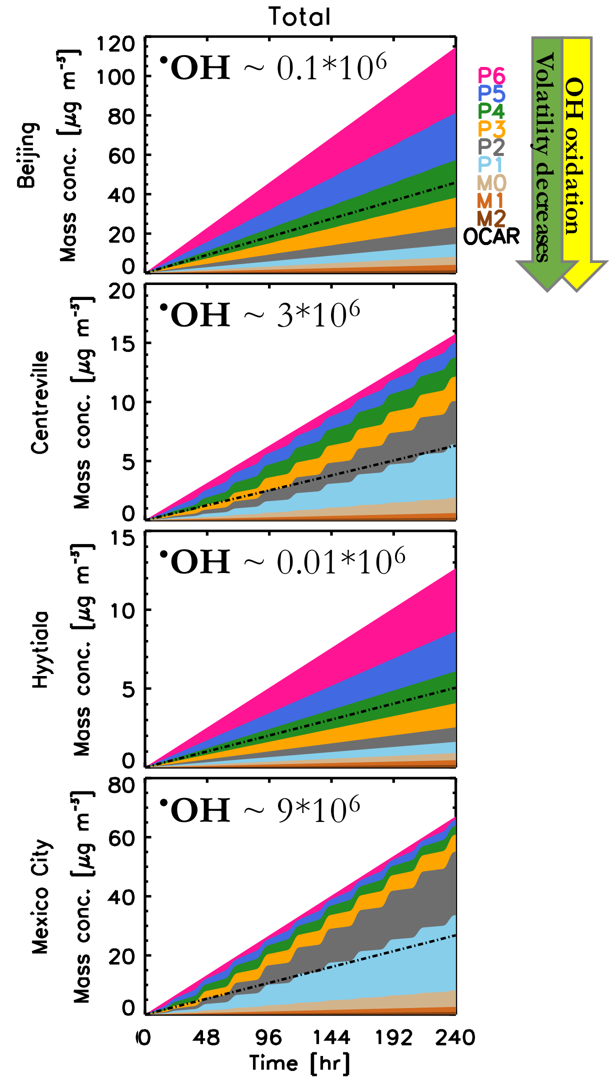
January

Similar distribution:
more high volatile species



January

Similar distribution:
more high volatile species

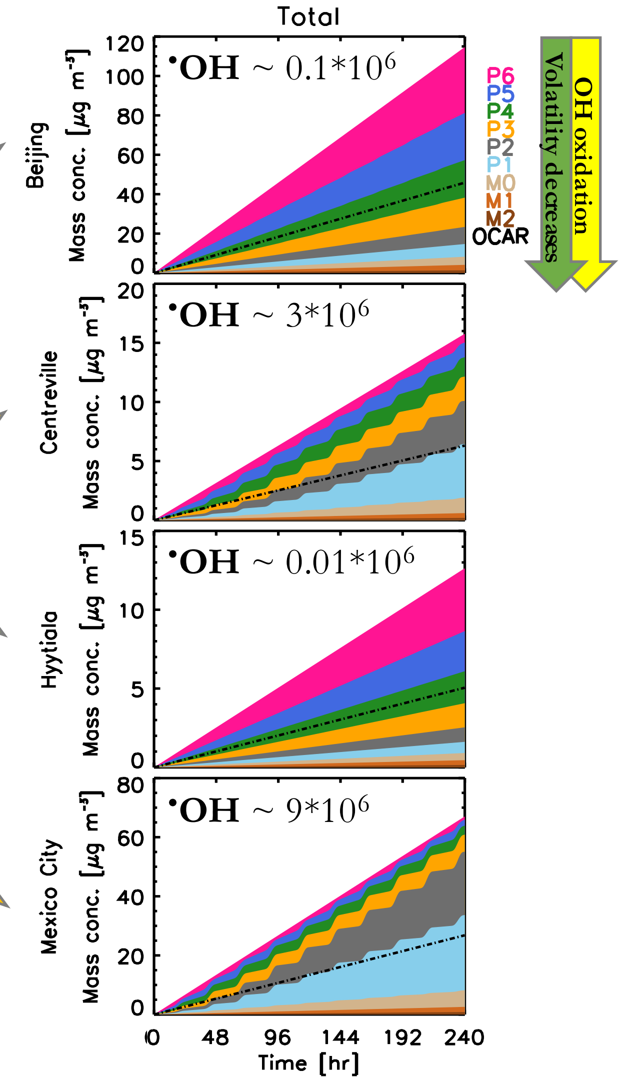


1. Box model development 2.Case Studies 3. Monte-Carlo 4.Simplification 5. Implement in GCM 6.GCM studies

January

Similar distribution:
more high volatile species

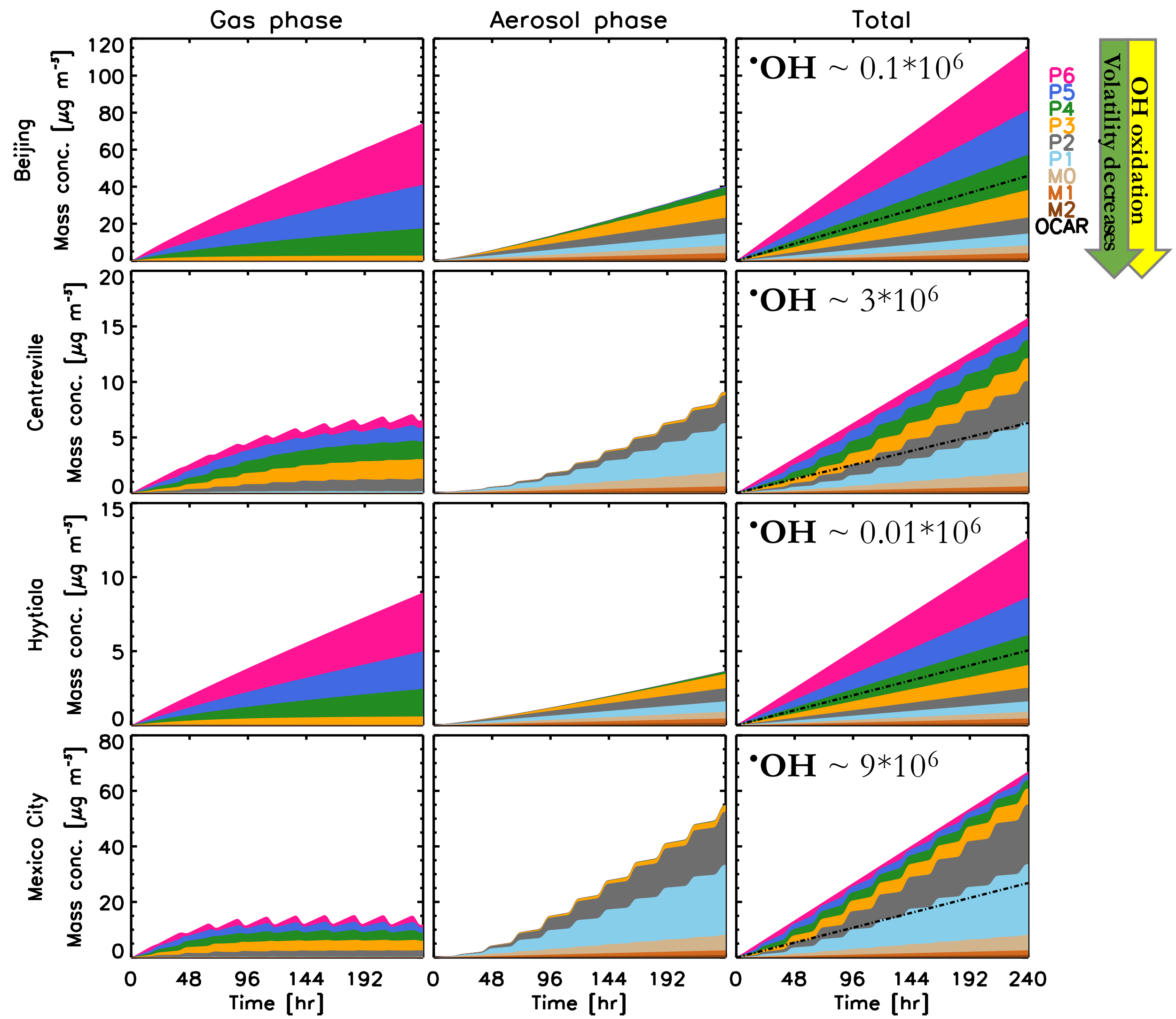
Diurnal variability



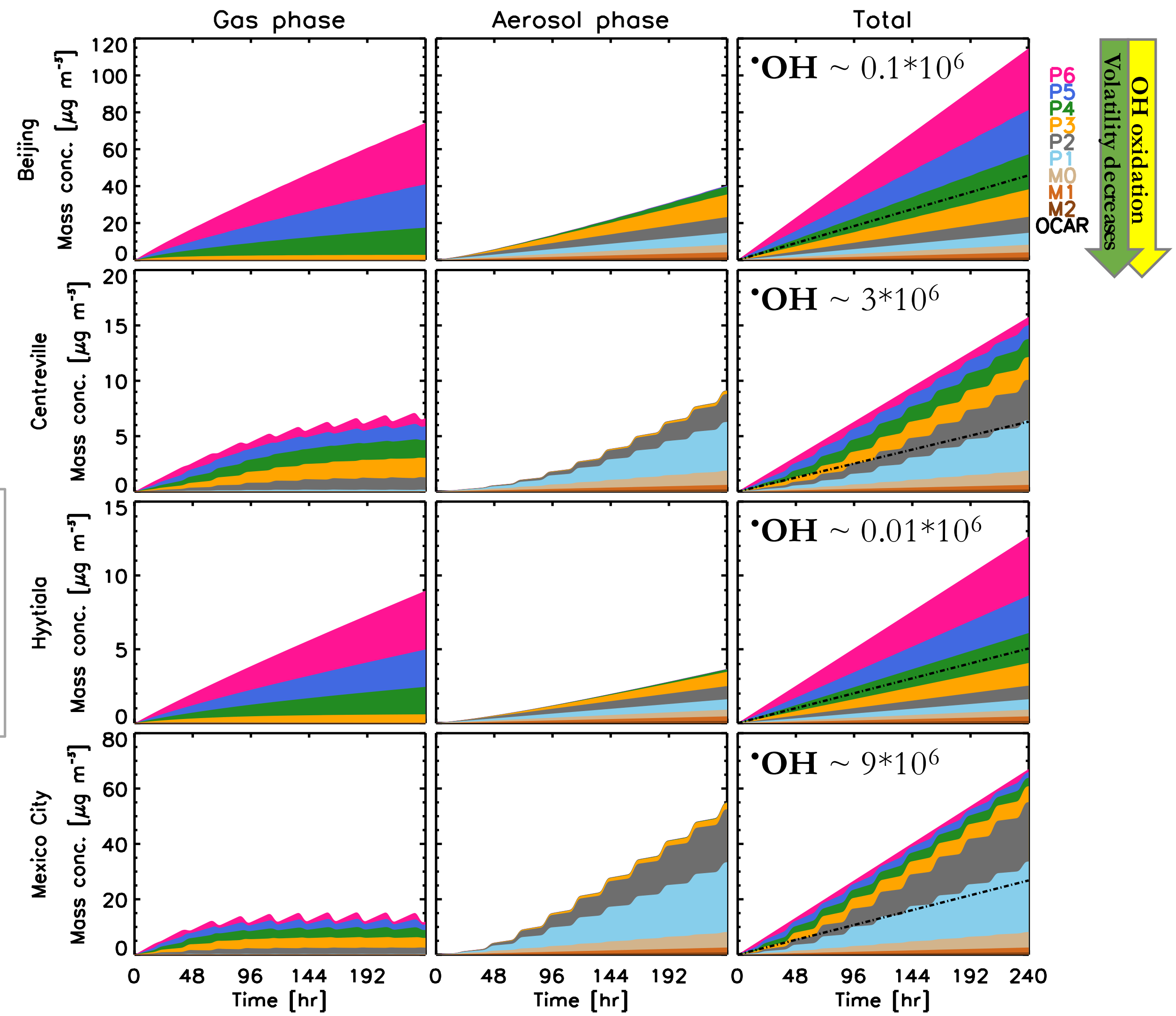
•OH determines oxidation
1) Volatility distribution
2) Diurnal variability

January

Low •OH,
less oxidation,
more high
volatility species,
more gas phase



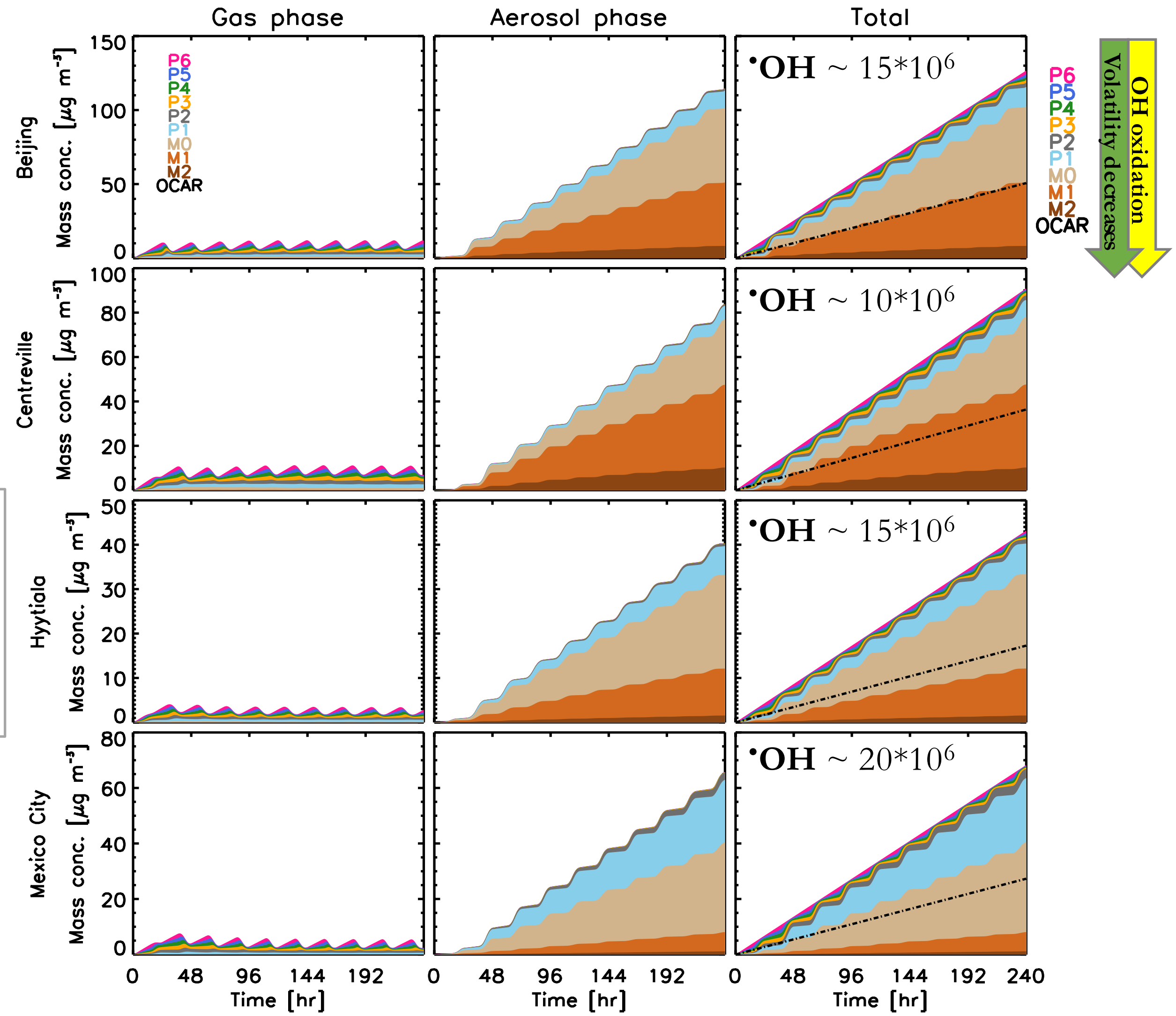
January



High •OH, more oxidation, diurnal variability, more low volatility species, more aerosol phase

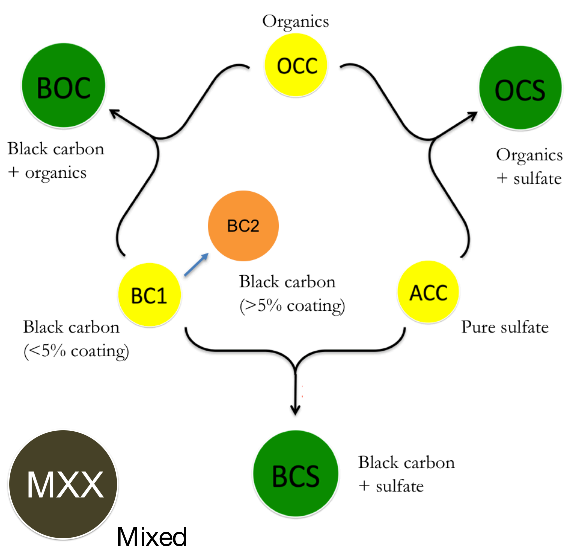
July

High •OH,
more oxidation,
diurnal variability,
more low volatility
species, more
aerosol phase

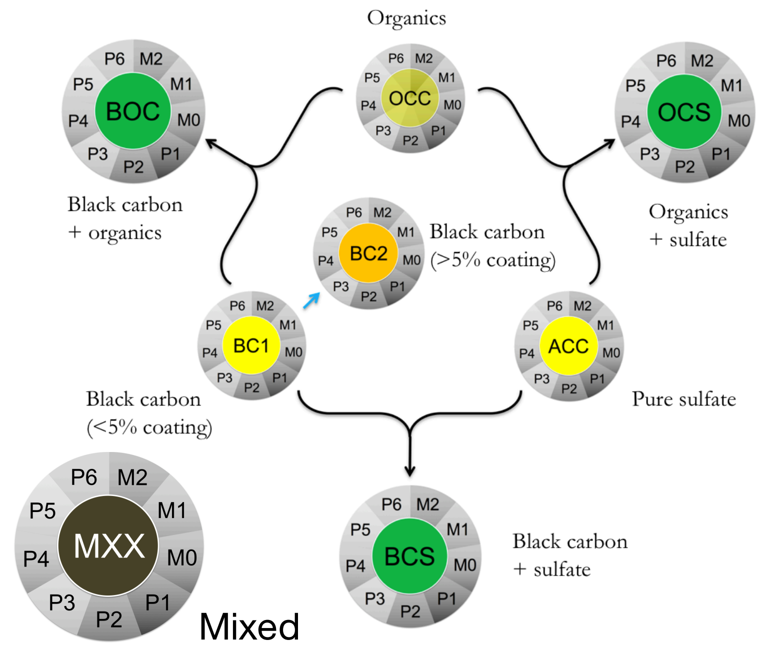


Organics grow via condensation in addition to coagulation in the new scheme.

MATRIX: coagulation



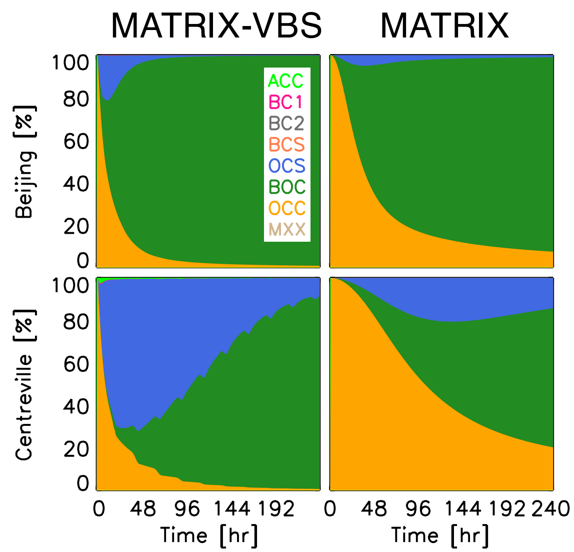
MATRIX-VBS: coagulation + condensation



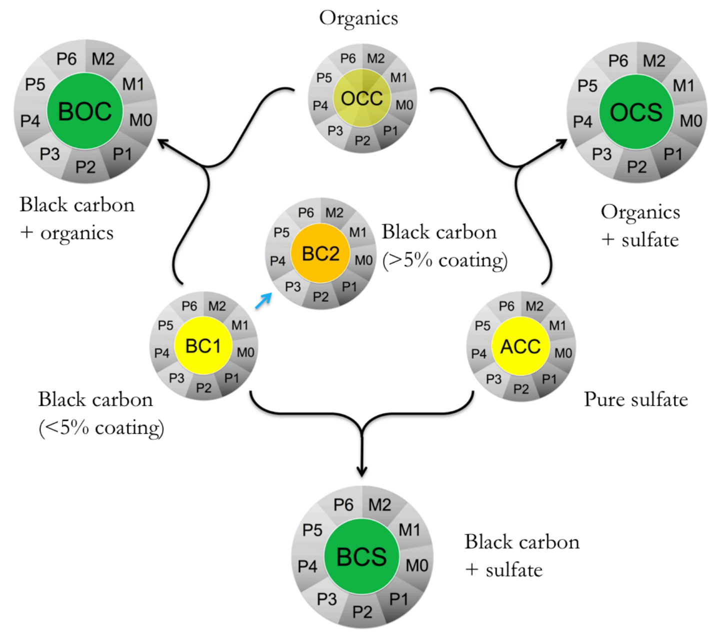
Yellow: emitted (donor)
Green: secondary (receiver)

Mixing states in the new and old schemes are different

Organic containing mass fraction in each population

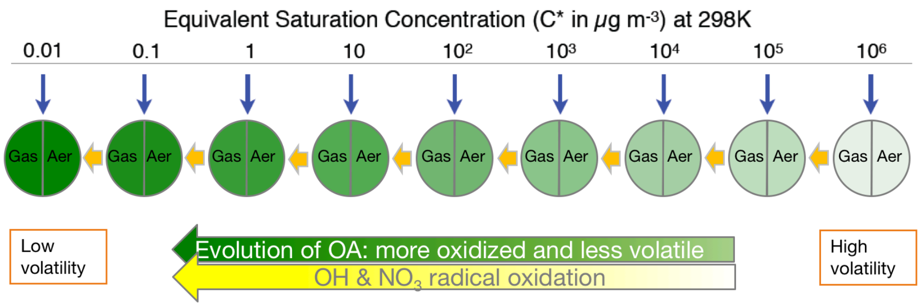


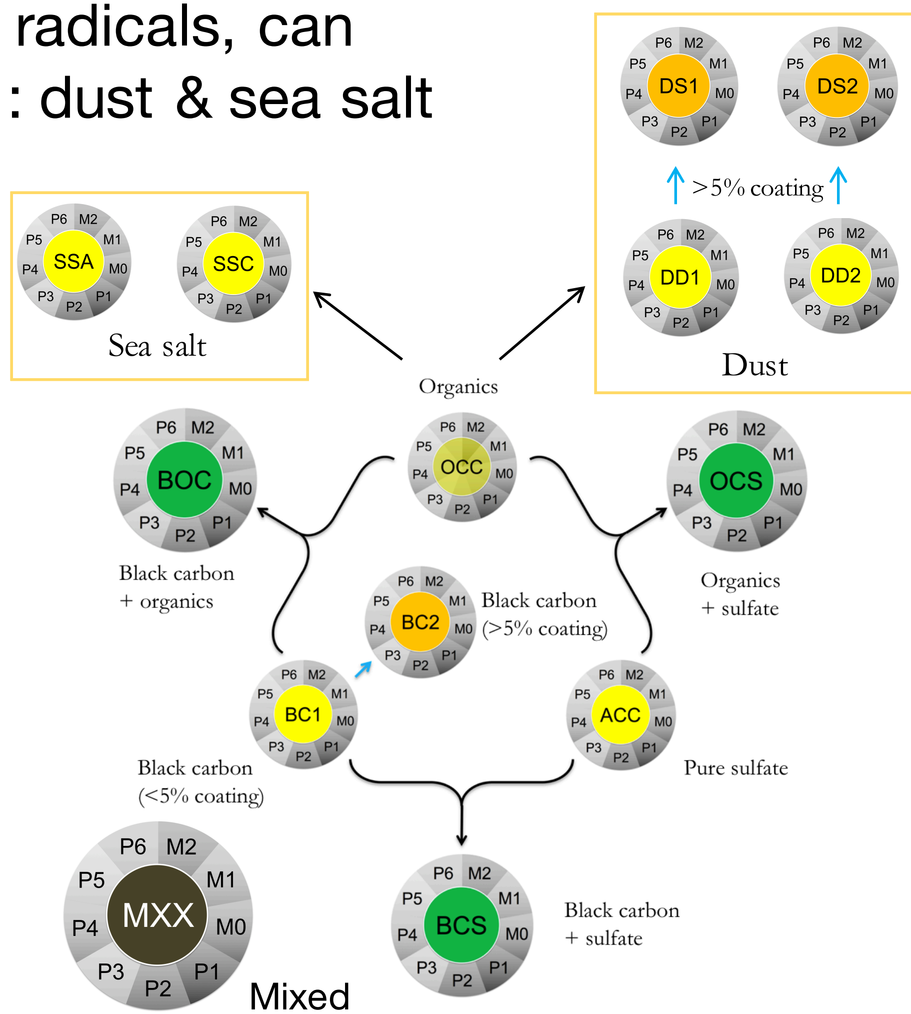
MATRIX-VBS: coagulation + condensation



1. Box model development 2.Case Studies 3. Monte-Carlo 4.Simplification 5. Implement in GCM 6.GCM studies

Organics can be oxidized by NO_3 radicals, can condense on coarse mode aerosols : dust & sea salt





Bonus: add NO_3 radical as oxidant, include organics in coarse mode aerosols

1. Box model development 2.Case Studies 3. Monte-Carlo 4.Simplification 5. Implement in GCM 6.GCM studies

The Monte-Carlo simulations cover all conditions possible

	T (K)	RH (%)	latitude	**Emissions of aerosols ($\mu g/m^3/s$)**							**Emissions of gases ($\mu g/m^3/s$)**				
											VOCs (in sets)				
				Sulfate (SO_2)*	**Organics**	**Black carbon**	**Dust (in pairs)**		**Sea salt (in pairs)**		Alkenes	Paraffin	Terpenes	Isoprene	NOx
	220	0.1	0	1.0E+5	5.0E-6	1.0E-6	1.0E-4	1.0E-4	1.0E-5	1.0E-4	5.0E+2	5.0E+3	1.0E+4	1.0E+4	1.0E+5
	230	20	30N/S	1.0E+6	5.0E-5	1.0E-5	1.0E-3	1.0E-3	5.0E-5	5.0E-4	5.0E+3	1.0E+4	1.0E+5	1.0E+5	1.0E+6
	240	40	60N/S	5.0E+6	5.0E-4	1.0E-4	5.0E-3	5.0E-3	1.0E-4	1.0E-3	5.0E+4	5.0E+4	1.0E+6	5.0E+6	1.0E+7
	250	60	90N/S												
range	260	80													
	270	100													
	280														
	290														
	300														
	310														

* 2.5 % of SO_2 mass is SO_4

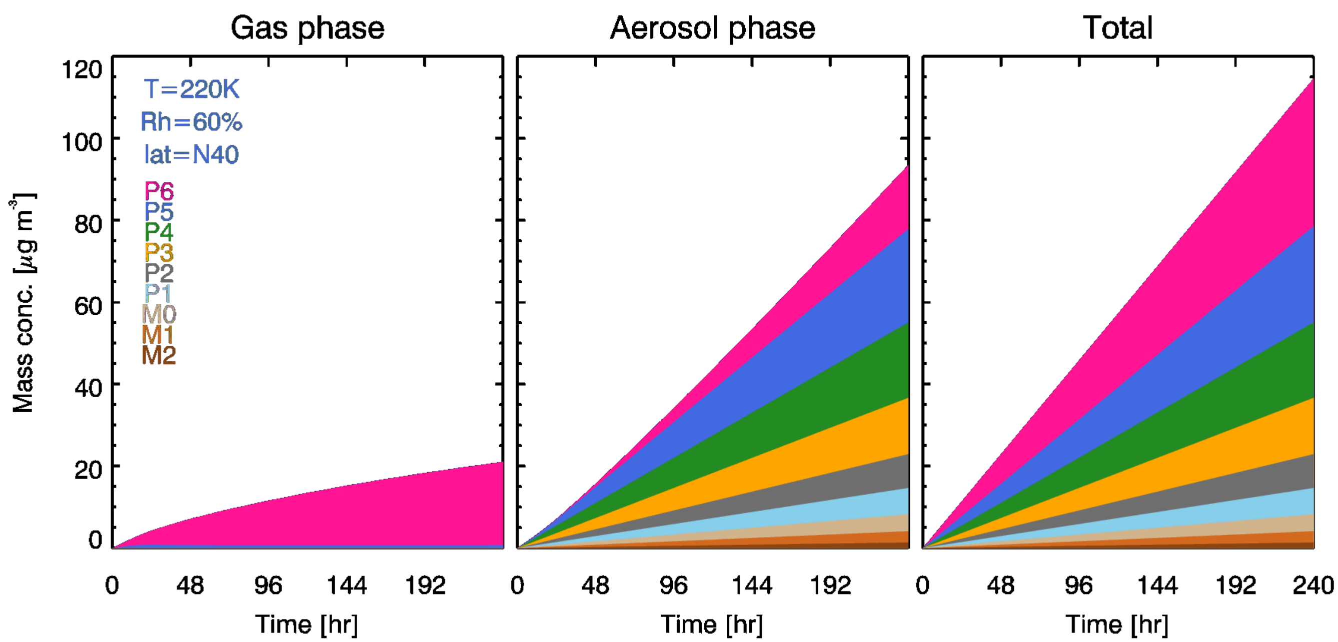
The Monte-Carlo simulations cover all conditions possible, in low, medium and high levels

	T (K)	RH (%)	latitude	Emissions of aerosols ($\mu g/m^3/s$)							Emissions of gases ($\mu g/m^3/s$)				
											VOCs (in sets)				
				Sulfate (SO_2)*	Organics	Black carbon	Dust (in pairs)		Sea salt (in pairs)		Alkenes	Paraffin	Terpenes	Isoprene	NOx
	220	0.1	0	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
	230	20	30N/S	MED	MED	MED	MED	MED	MED	MED	MED	MED	MED	MED	MED
	240	40	60N/S	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH
	250	60	90N/S												
	260	80													
range	270	100													
	280														
	290														
	300														
	310														

* 2.5 % of SO_2 mass is SO_4

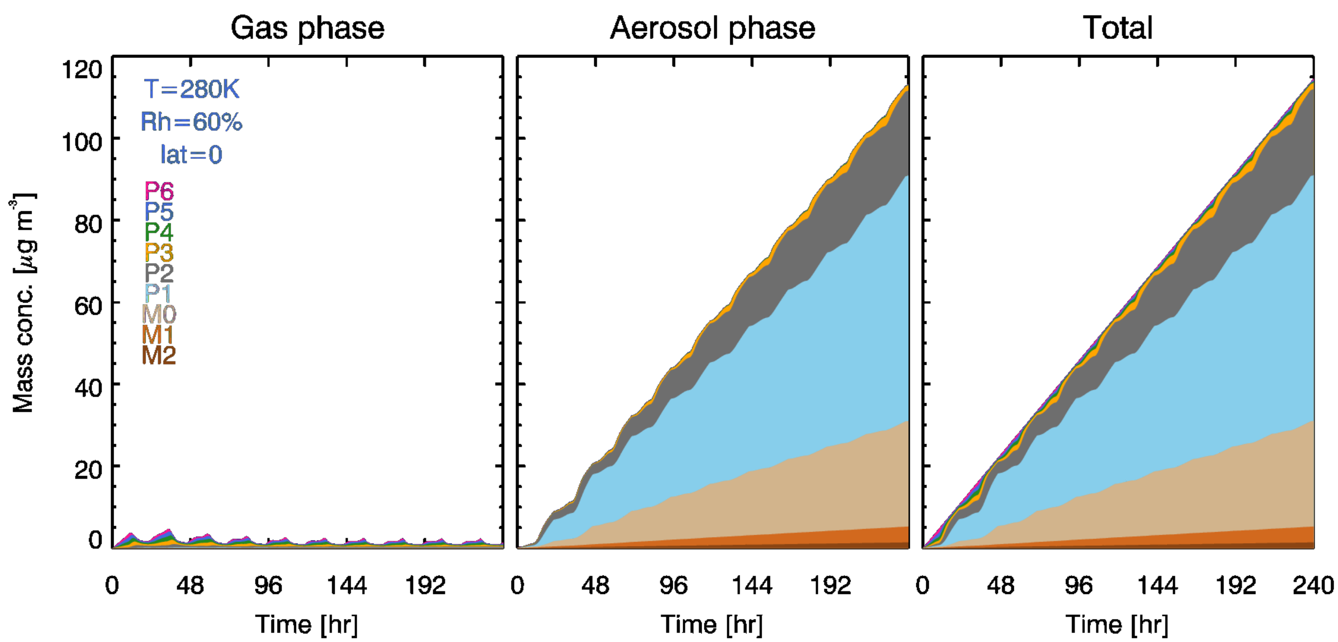
That's $10 \times 6 \times 7 \times 3^5 \times 3^2 = 918{,}540$ simulations !!

Change **temperature** and keep everything else constant



- Volatility has a temperature dependence.
- Less volatile, higher vaporization enthalpies, more volatile, lower vaporization enthalpies.
- High T organics partition to the gas phase, low T to the aerosol phase.

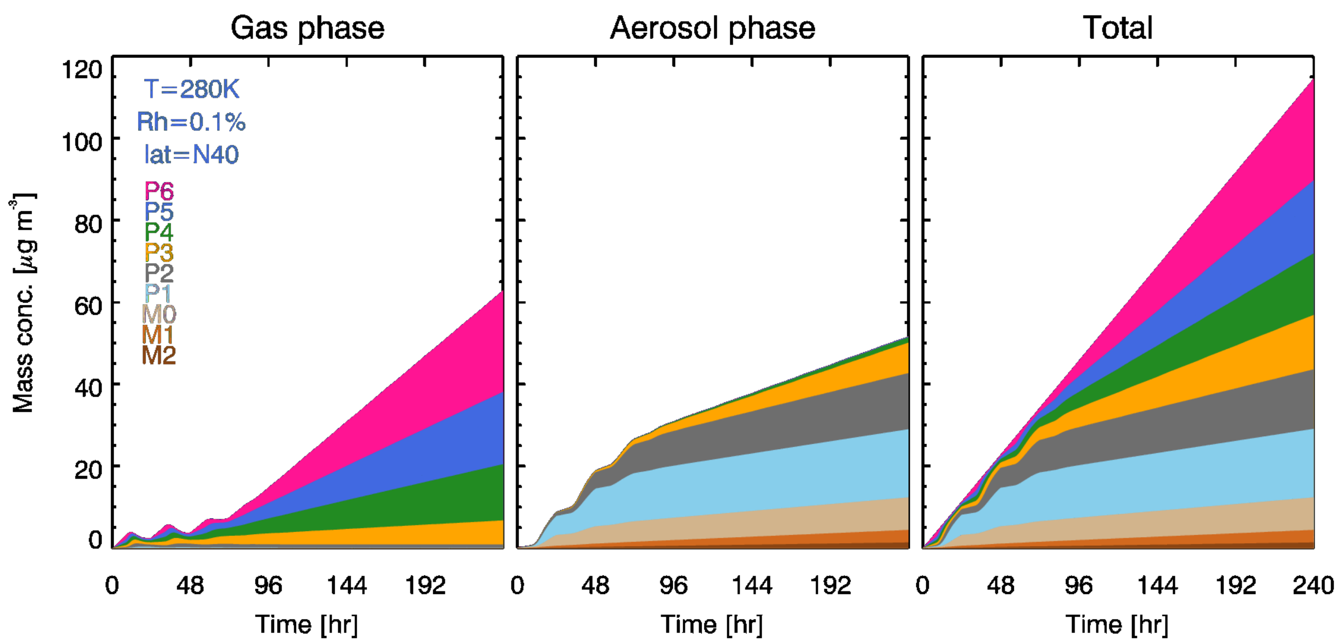
Change **latitude** and keep everything else constant



- 30N~70S distinctively more aerosol phase OC, more sunlight, more photolysis, more OH radicals, more oxidation.
- 90N~30N and 70S~90S comparable or more gas phase OC.

$O_3 + hv \rightarrow O^1D + O_2$
$O^1D + H_2O \rightarrow 2OH$

Change **relative humidity (RH)** and keep everything else constant

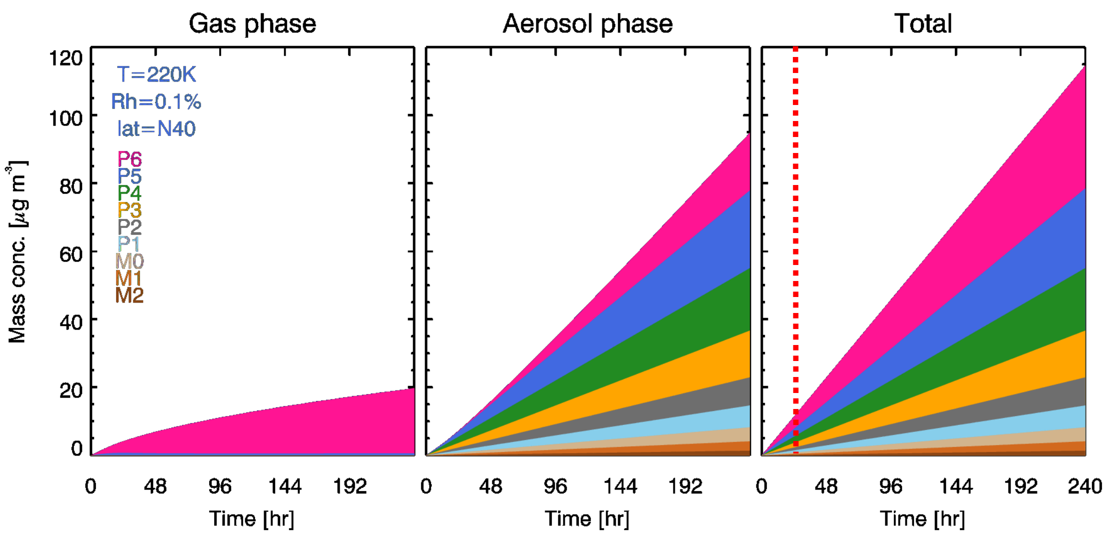


- Higher RH, more H_2O, more OH formed, more oxidation, more to the aerosol phase.

$O_3 + h\nu \rightarrow O^1D + O_2$

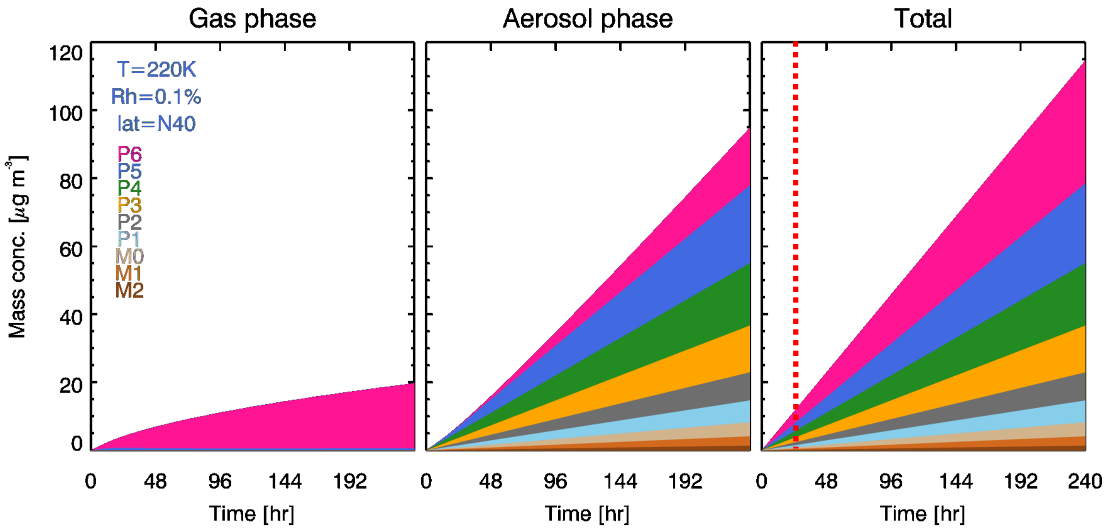
$O^1D + H_2O \rightarrow 2OH$

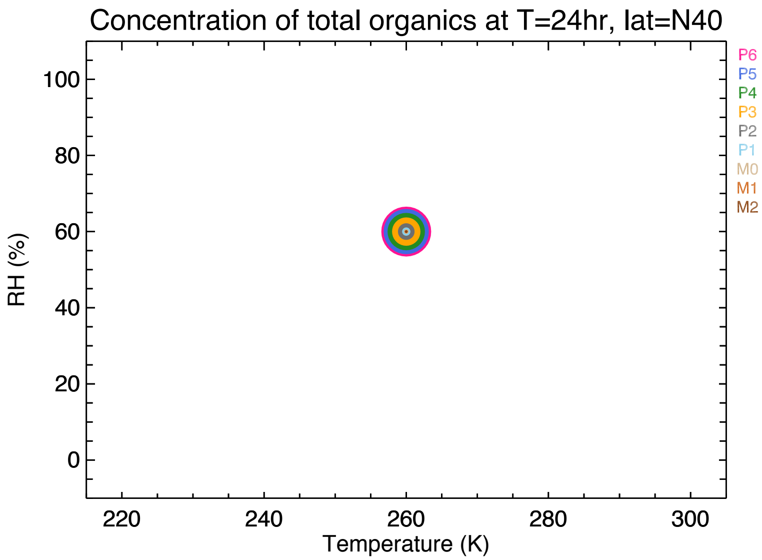
Change **temperature** and **relative humidity**



- Take a snapshot at 24hr

Change **temperature** and **relative humidity**

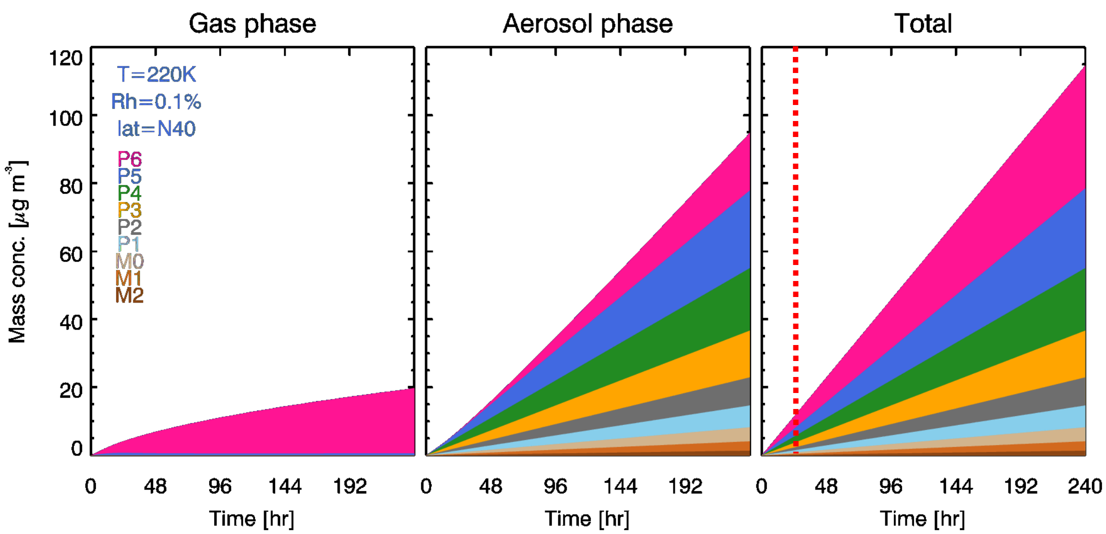


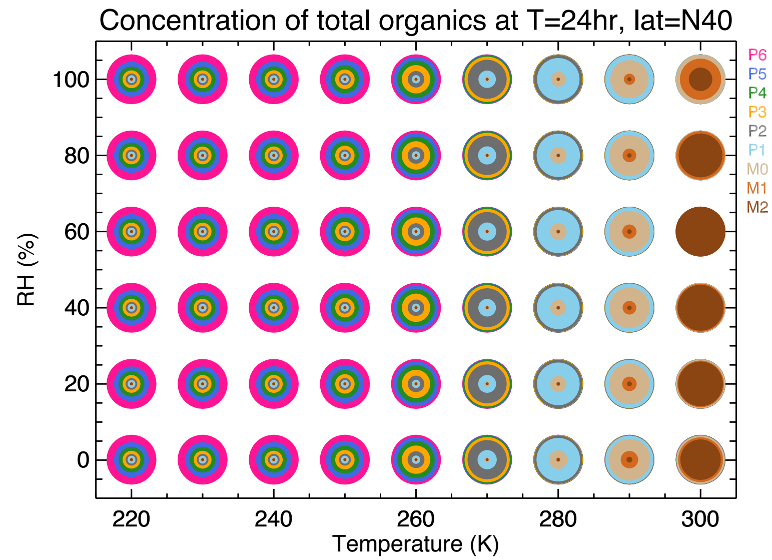


Size of the circle: the concentration of organics
Color: their volatility

- Take a snapshot at 24hr
- Look at organics concentration with respect to RH and T

Change **temperature** and **relative humidity**

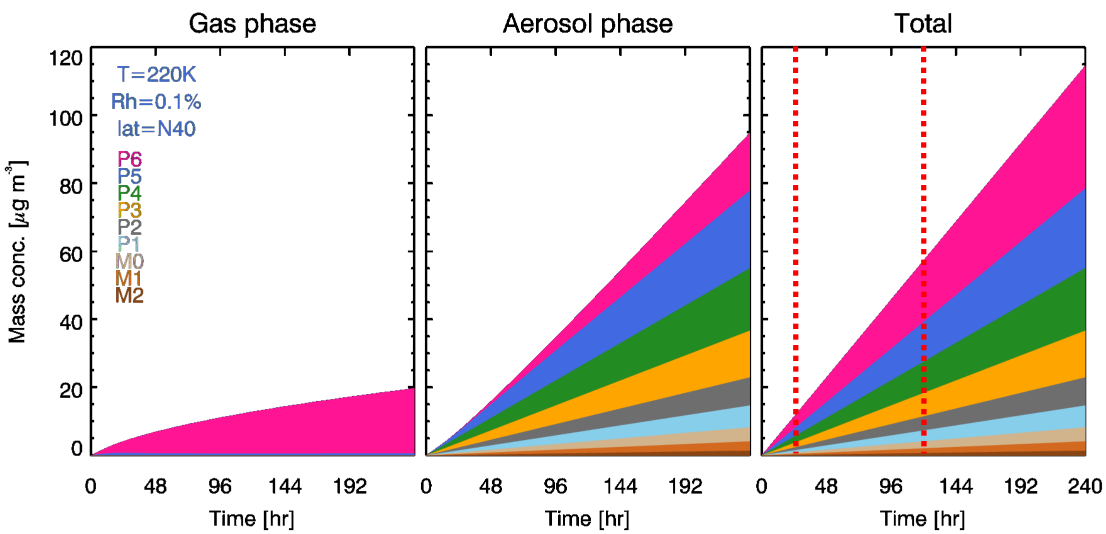


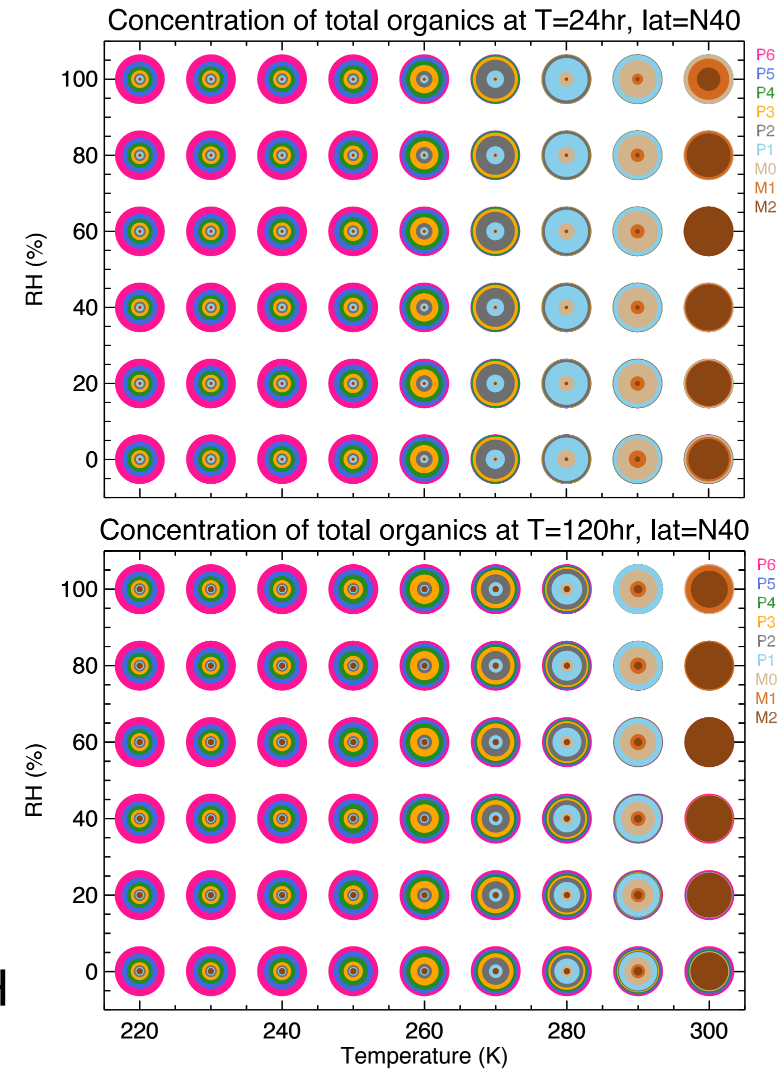


Size of the circle: the concentration of organics
Color: their volatility

- Take a snapshot at 24hr
- Look at organics concentration with respect to RH and T

Change **temperature** and **relative humidity**

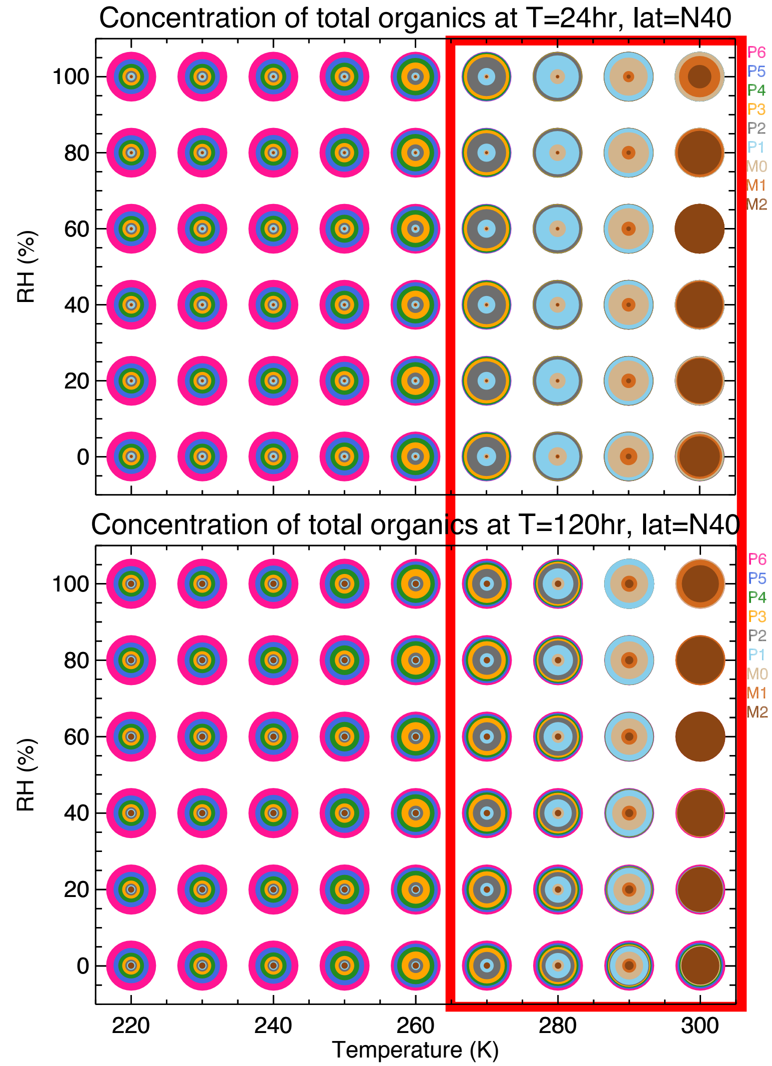




- Take 2 snapshots at 24hr and 120hr
- Look at organics concentration with respect to RH and T

- Different distributions of volatilities in the red box:
    - At 24hr, no more high volatile species
    - At 120hr, still some high volatile species
- Why?
    - OH is different!

- More OH, more oxidation, more low volatile species



- Different distributions of volatilities in the red box:
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  - At 120hr, still some high volatile species
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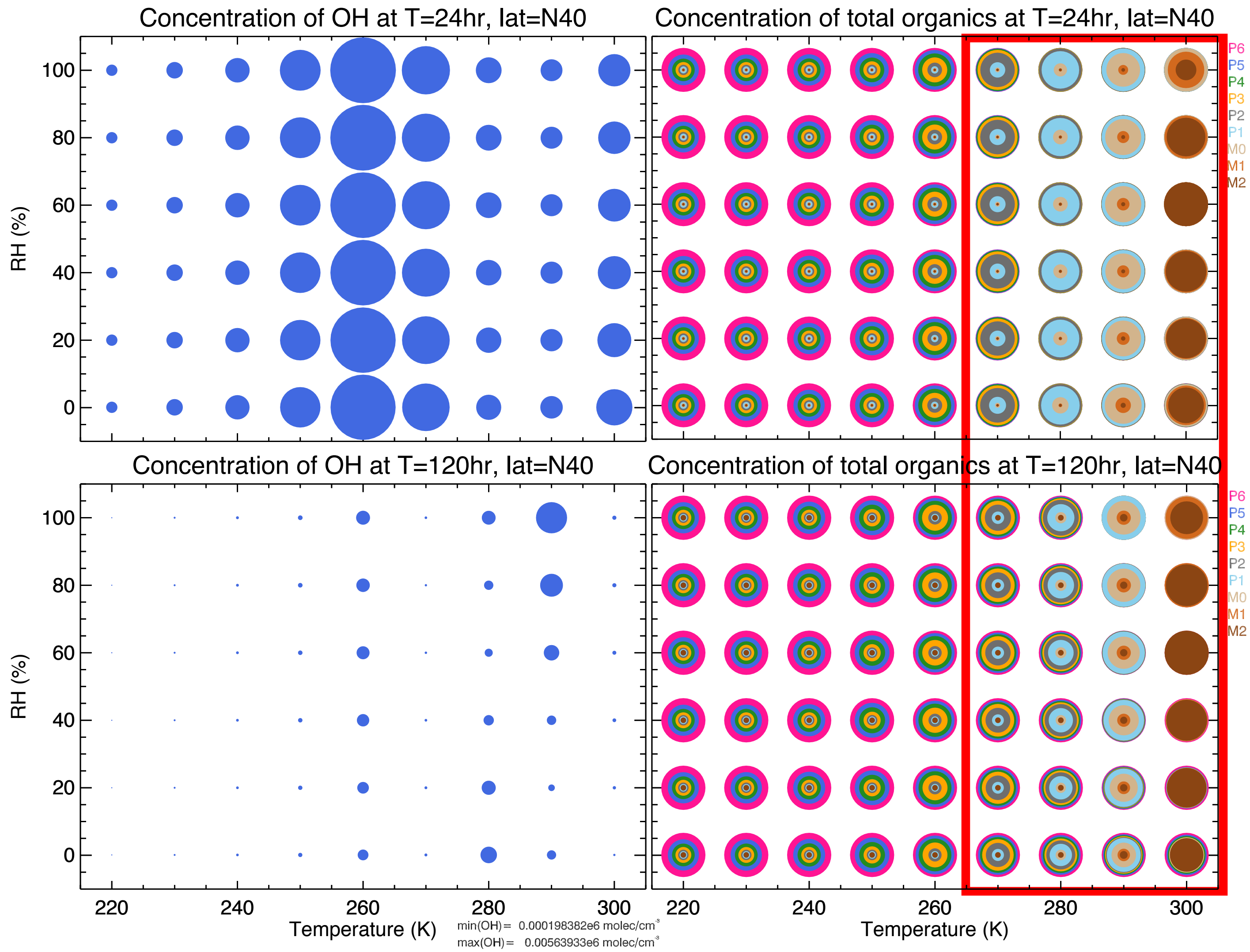
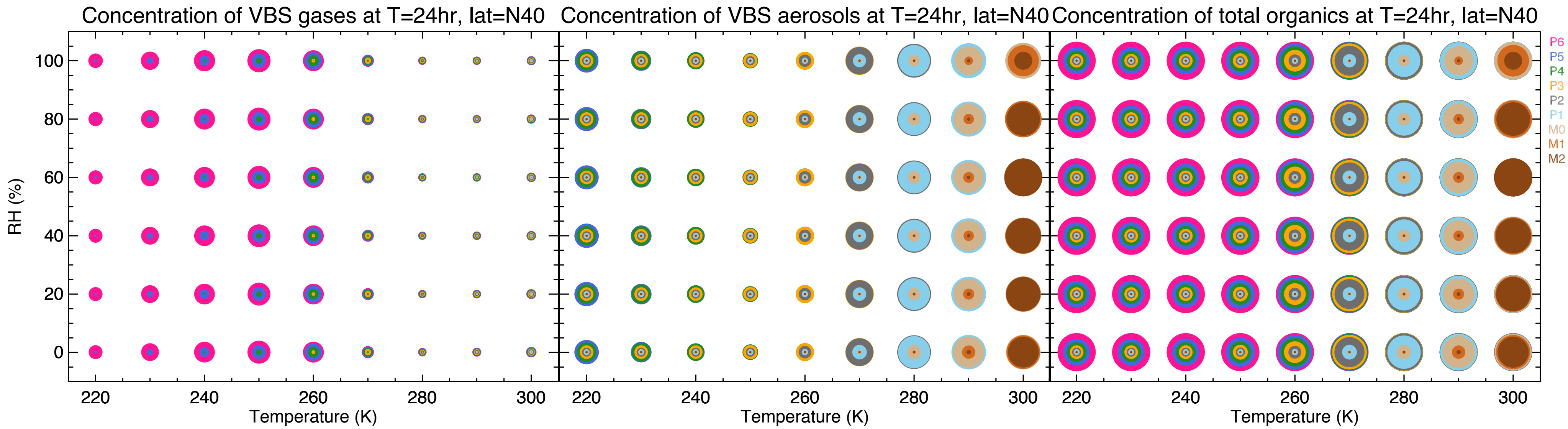
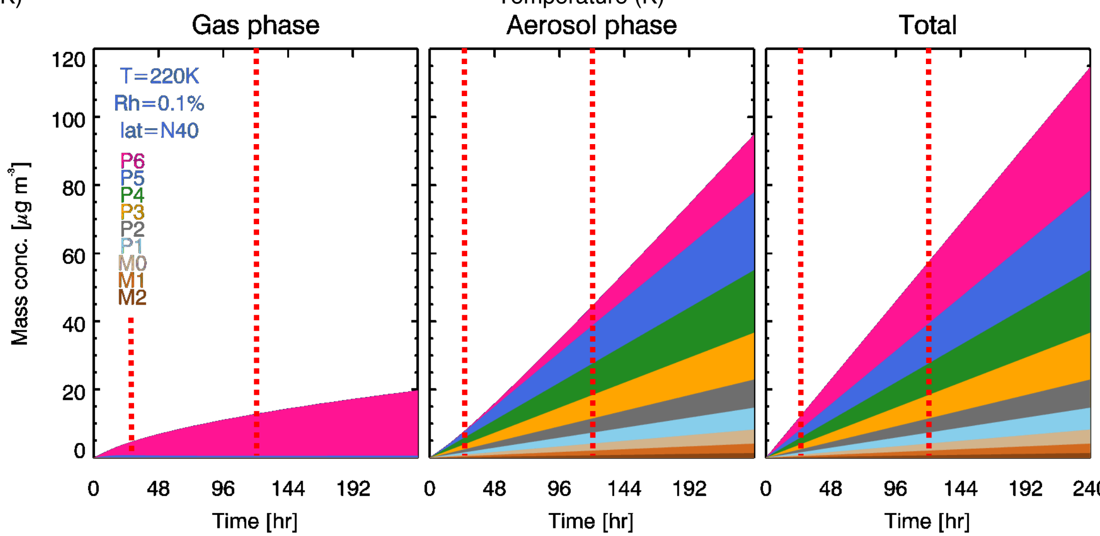






1. Box model development 2.Case Studies 3. Monte-Carlo 4.Simplification 5. Implement in GCM 6.GCM studies

Change **aerosol emissions**, alter mixing states

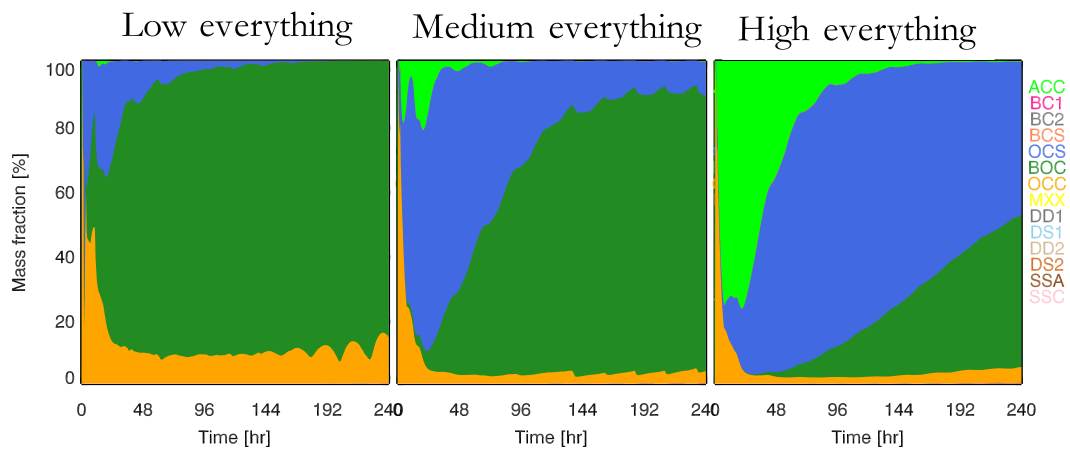
Emissions of aerosols ($\mu g/m^3/s$)

Sulfate (SO_2)*	Organics	Black carbon	Dust (in pairs)		Sea salt (in pairs)	
LOW	LOW	LOW	LOW	LOW	LOW	LOW
MED	MED	MED	MED	MED	MED	MED
HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH

Change **aerosol emissions**, alter mixing states

Emissions of aerosols (µg/m³/s)

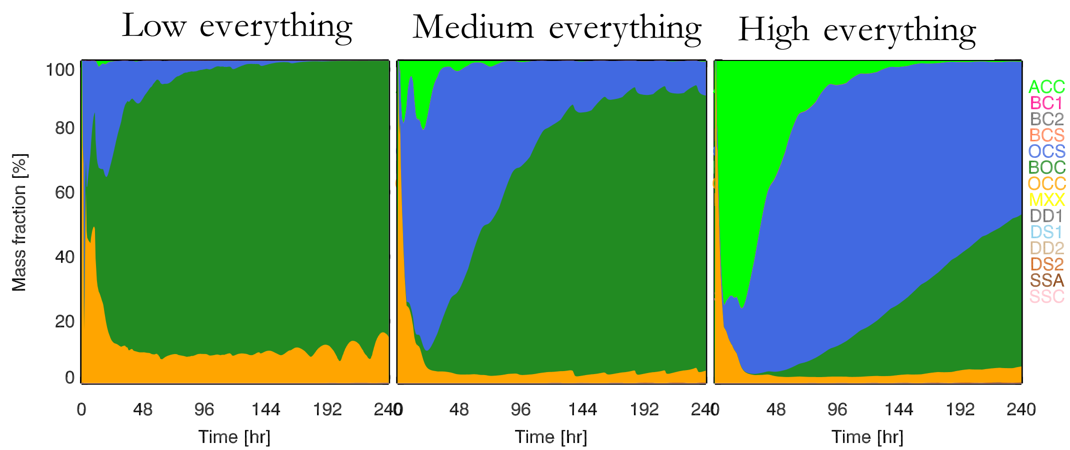
Sulfate (SO_2)*	Organics	Black carbon	Dust (in pairs)		Sea salt (in pairs)	
LOW	LOW	LOW	LOW	LOW	LOW	LOW
MED	MED	MED	MED	MED	MED	MED
HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH

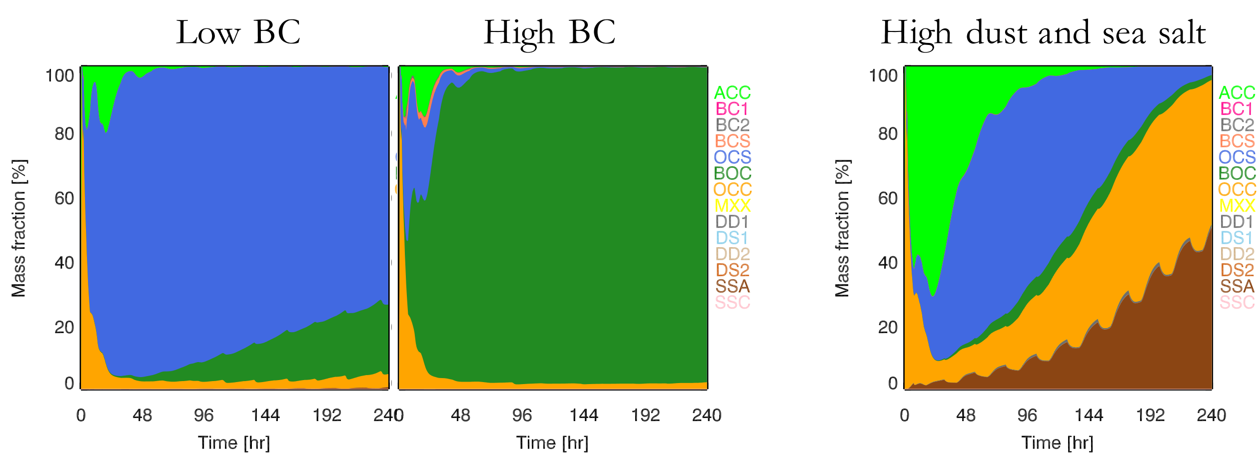


Change **aerosol emissions**, alter mixing states

Emissions of aerosols (µg/m^3/s)

Sulfate (SO_2)*	Organics	Black carbon	Dust (in pairs)		Sea salt (in pairs)	
LOW	LOW	LOW	LOW	LOW	LOW	LOW
MED	MED	MED	MED	MED	MED	MED
HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH





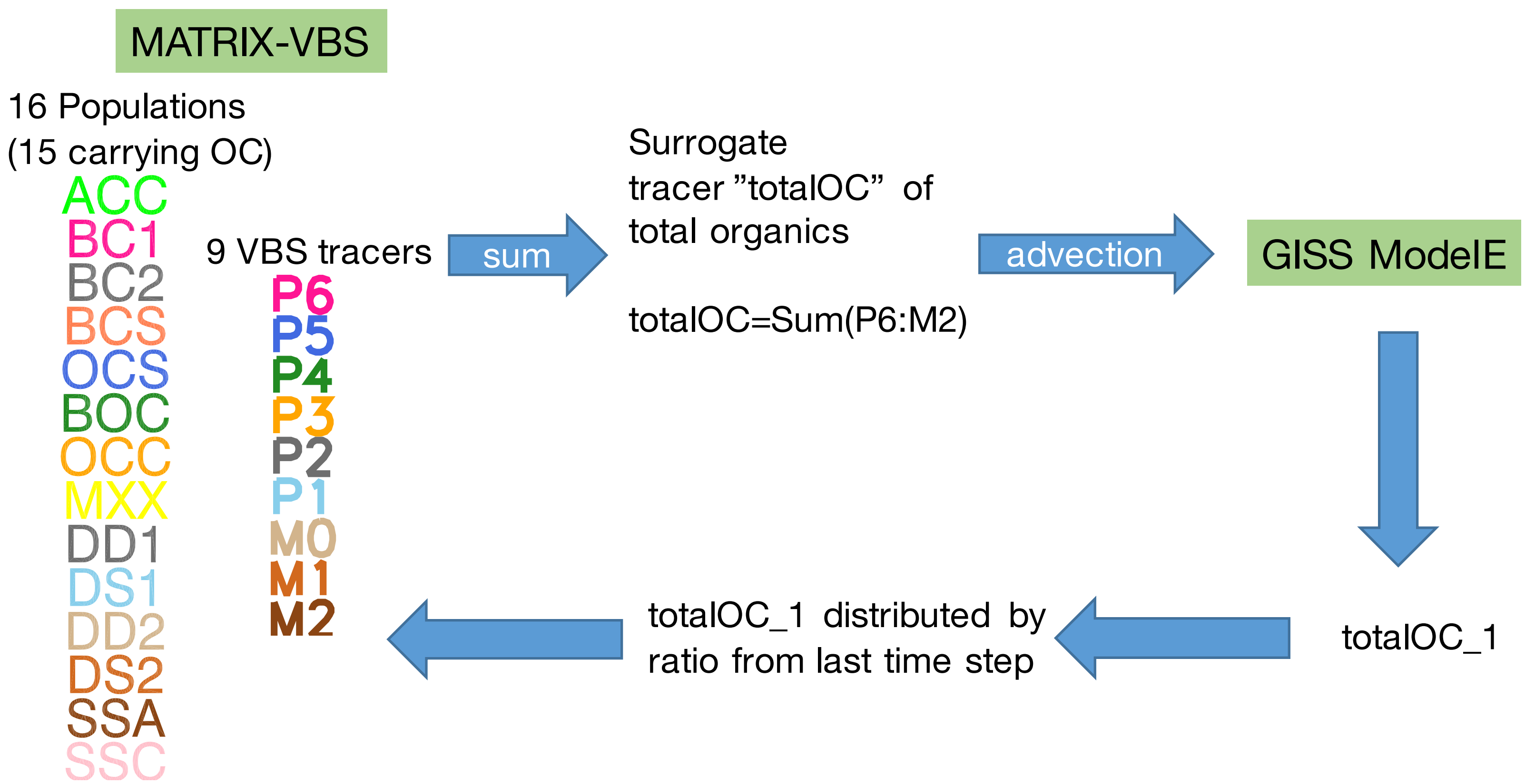
The Monte-Carlo simulations cover all conditions possible, in low, medium and high levels

	T (K)	RH (%)	latitude	Emissions of aerosols ($\mu g/m^3/s$)							Emissions of gases ($\mu g/m^3/s$)				
				Sulfate (SO_2)*	Organics	Black carbon	Dust (in pairs)		Sea salt (in pairs)		VOCs (in sets)				NOx
											Alkenes	Paraffin	Terpenes	Isoprene	
range	220	0.1	0	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
	230	20	30N/S	MED	MED	MED	MED	MED	MED	MED	MED	MED	MED	MED	MED
	240	40	60N/S	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH
	250	60	90N/S												
	260	80													
	270	100													
	280														
	290														
	300														
	310														

* 2.5 % of SO_2 mass is SO_4

That's $10\times6\times7\times3^5\times3^2=918{,}540$ simulations !!

Simplification 1: transport total organics in the GCM

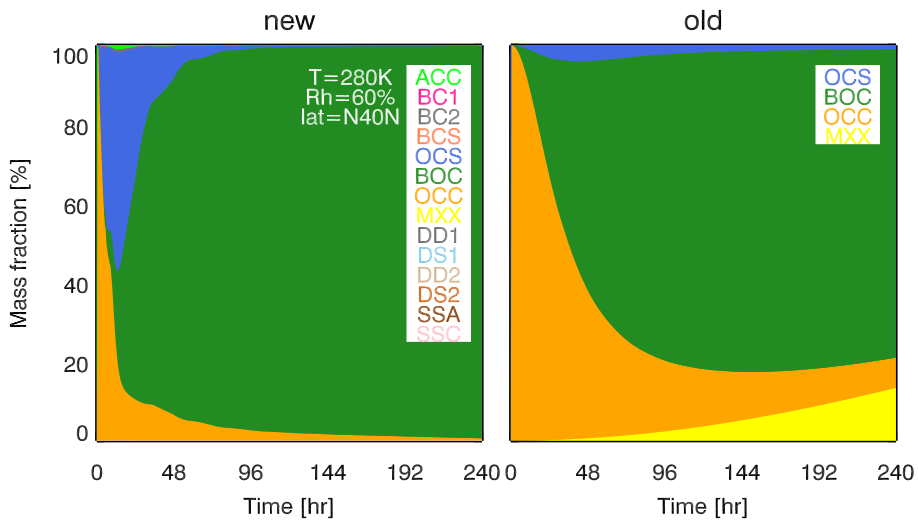


Simplification 2: reduce populations carrying organics

Emissions of aerosols (µg/m^3/s)

Sulfate (SO_2)*	**Organics**	**Black carbon**	**Dust (in pairs)**		**Sea salt (in pairs)**	
LOW	LOW	LOW	LOW	LOW	LOW	LOW
MED	MED	MED	MED	MED	MED	MED
HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH

Mixing states, how do they change?
Are some populations not really populated?



Create interface.

Compare size-resolved number concentrations with 11 global aerosol microphysics models of different complexity [*Mann et al.,* 2014]

Model	Scheme type	Classes	Multi-dist	Tracers	Host model	Resolution	Reference
CAM5-MAM3	modal (2 m)	3	N	15	GCM (free)	$1.9° \times 2.5° \times$ L30	Liu et al. (2012)
HadGEM3-UKCA	modal (2 m)	5	Y	20	GCM (nudg)	$1.3° \times 1.9° \times$ L63	Mann et al. (2014)
TM5	modal (2 m)	7	Y	25	CTM	$2.0° \times 3.0° \times$ L34	Aan de Brugh et al. (2011)
GLOMAP-mode	modal (2 m)	7	Y	26	CTM	$2.8° \times 2.8° \times$ L31	Mann et al. (2012)
EMAC	modal (2 m)	7	Y	41	GCM (nudg)	$2.8° \times 2.8° \times$ L19	Pringle et al. (2010)
ECHAM5-HAM2	modal (2 m)	7	Y	29(a)	GCM (nudg)	$1.9° \times 1.9° \times$ L31	Zhang et al. (2012)
GISS-MATRIX	modal[b] (2 m)	16	Y	60	GCM (nudg)	$2.0° \times 2.5° \times$ L40	Bauer et al. (2008)
CanAM4-PAM	pcwise-lgnrml (2 m)	7	N	20	GCM (free)	$3.7° \times 3.7° \times$ L35	von Salzen (2006)
GEOS-Chem-APM	mode & sect. (1 m)	100	Y	100	CTM	$2.0° \times 2.5° \times$ L47	Yu and Luo (2009)
ECHAM5-SALSA	sectional (2 m)	20	Y	65	GCM (nudg)	$1.9° \times 1.9° \times$ L31	Bergman et al. (2012)
GISS-TOMAS	sectional (2 m)	12	N	72	GCM (free)	$4.0° \times 5.0° \times$ L09	Lee and Adams (2010)
GLOMAP-bin	sectional (2 m)	40	Y	160	CTM	$2.8° \times 2.8° \times$ L31	Spracklen et al. (2005a, 2011)

Compare size-resolved number concentrations with observational data from *Mann et al.*, 2014

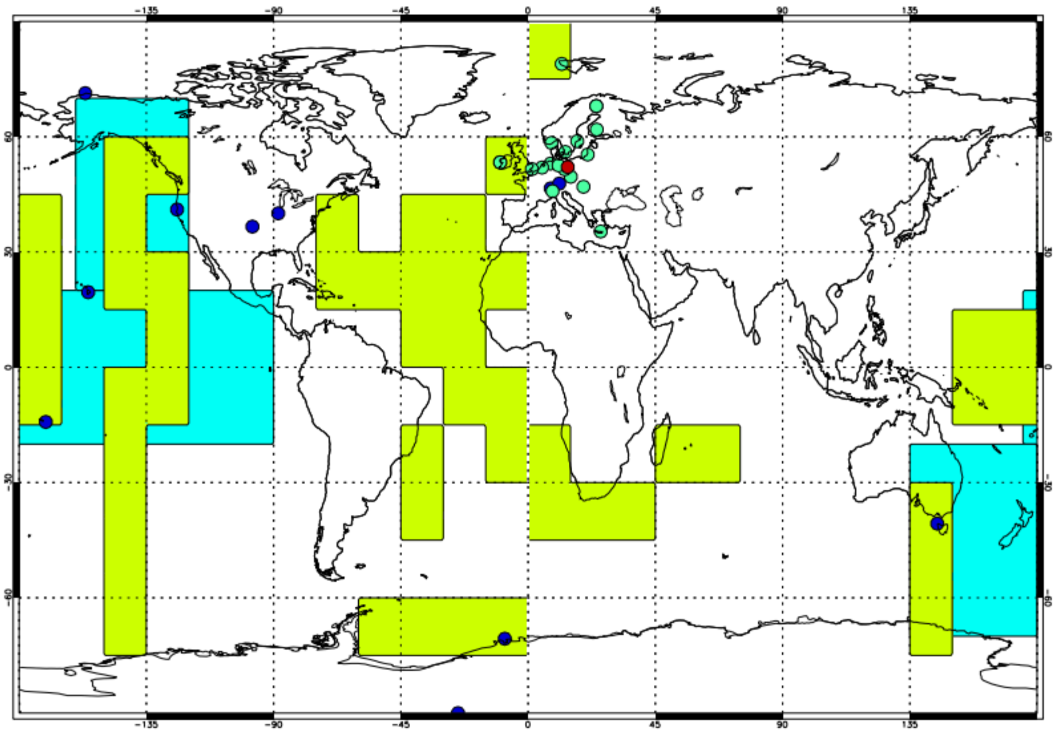


Figure 5. Global map indicating the locations of the measurement data sets shown in Table 3. Coloured circles show GAW-WDCA stations (blue), EUSAAR/GUAN supersites (aqua) and the location of the LACE 98 field campaign (red). The aqua boxed regions indicate where the aircraft field campaign measurements compiled in Clarke and Kapustin (2002) were made. The yellow boxed regions show the locations of the cruise campaign measurements compiled by Heintzenberg et al. (2000). When comparing to the measurements, each of the models was sampled based on a mask or interpolation to these locations.

Compare organics mass concentration with datasets from the AeroCom organic aerosol inter-comparison [*Tsigaridis et al*., 2014]

31 models

# of OA tracers : 1 – 62

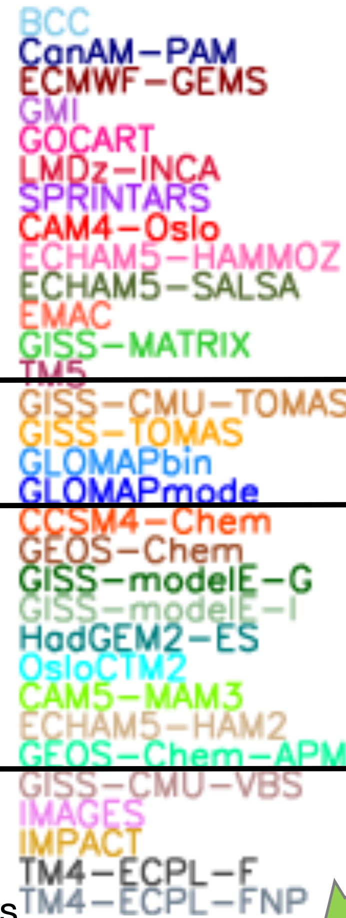
# of SOA tracers: 0 - 22

Very simple SOA:
non-volatile, emitted

Very simple SOA:
non-volatile, chemically produced

Explicit SOA:
semi-volatile, chemically produced

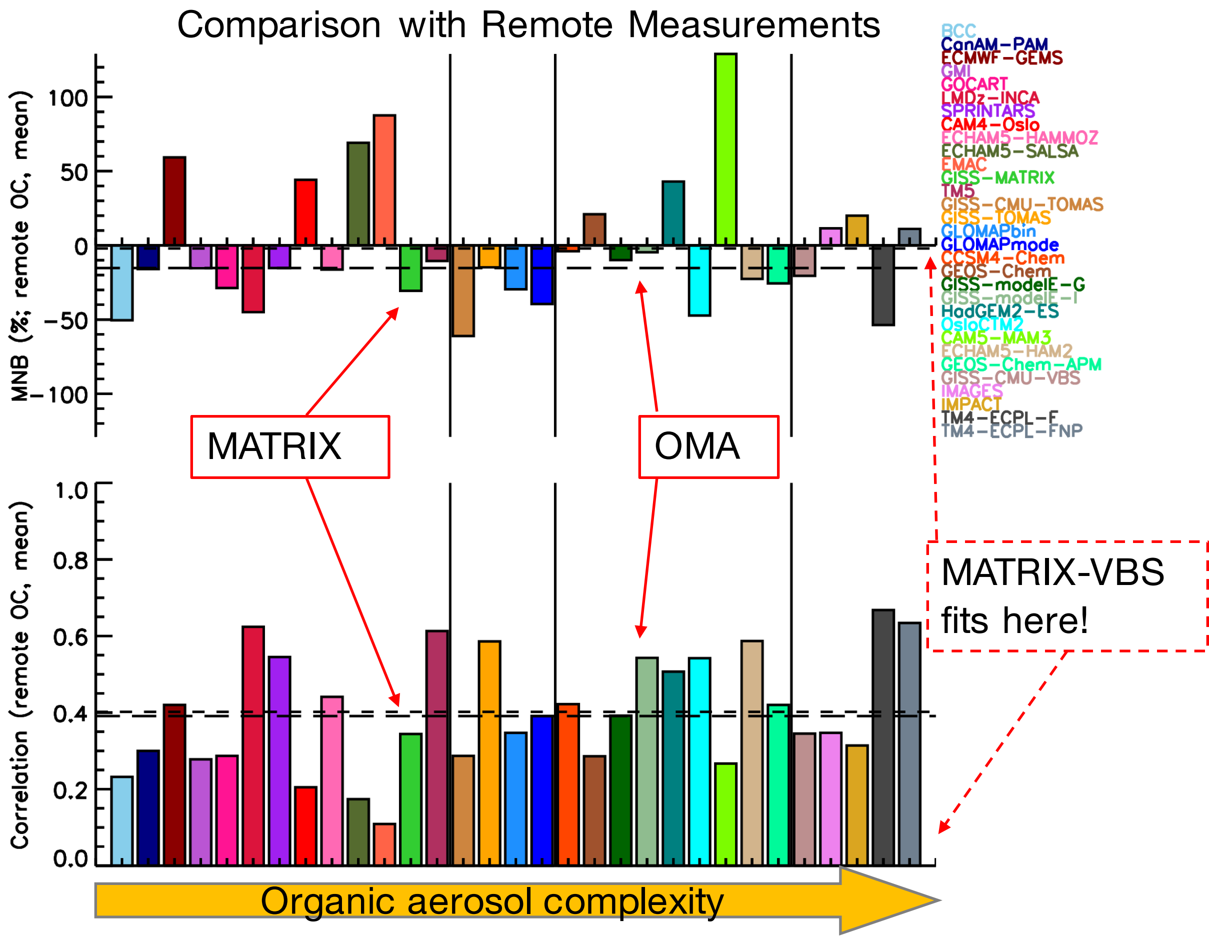
Explicit SOA:
semi-volatile, chemically produced
Include non-traditional SOA sources



Insert MATRIX-VBS here!

1. Box model development 2.Case Studies 3. Monte-Carlo 4.Simplification 5. Implement in GCM 6.GCM studies

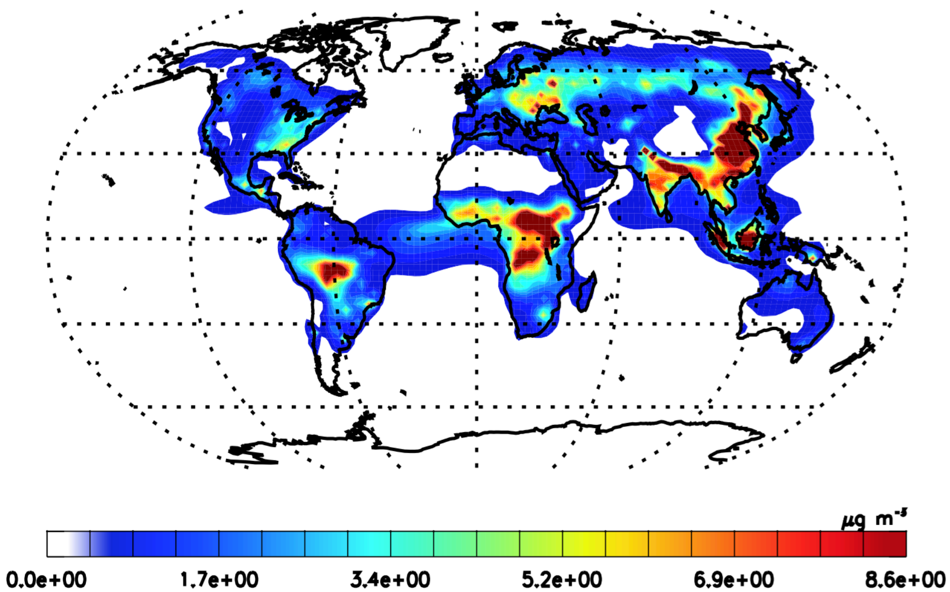
Compare organics mass concentration with datasets from the AeroCom organic aerosol inter-comparison [*Tsigaridis et al*., 2014]



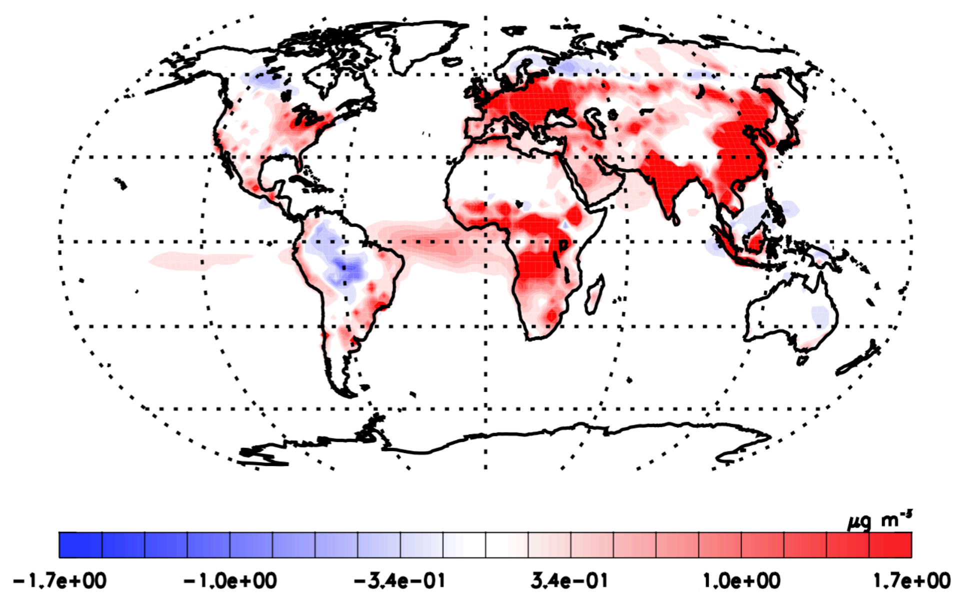
MATRIX-VBS will be compared to other aerosol schemes in GISS ModelE

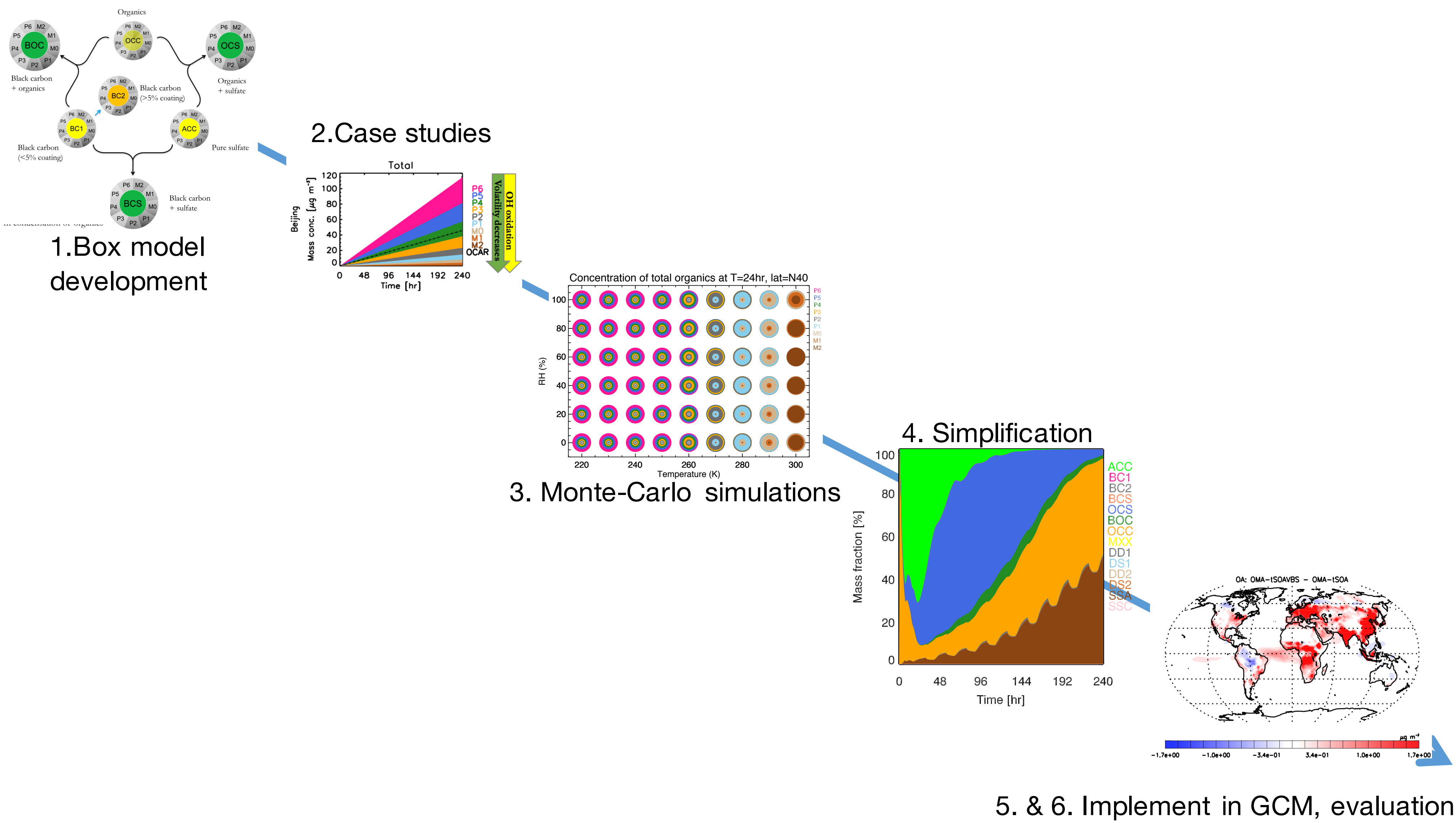
Model	Aerosol microphysics	Semi-volatile organics
OMA (one-moment aerosol)	✗	✗
OMA-VBS	✗	✓
MATRIX	✓	✗
MATRIX-VBS	✓	✓

Organic aerosol mass distribution in the OMA scheme



Difference between OA mass distribution in the OMA scheme and the OMA-VBS scheme





Organics
OCC
BOC
OCS
Black carbon + organics
Organics + sulfate
BC2
Black carbon (>5% coating)
BC1
ACC
Black carbon (<5% coating)
Pure sulfate
BCS
Black carbon + sulfate
1.Box model development
2.Case studies
Total
Beijing
Mass conc. [µg m⁻³]
Time [hr]
P6
P5
P4
P3
P2
P1
M0
M1
M2
OCAR
Volatility decreases
OH oxidation
Concentration of total organics at T=24hr, lat=N40
RH (%)
Temperature (K)
3. Monte-Carlo simulations
4. Simplification
Mass fraction [%]
Time [hr]
ACC
BC1
BC2
BCS
OCS
BOC
OCC
MXX
DD1
DS1
DD2
DS2
SSA
SSC
OA: OMA-tSOAVBS - OMA-tSOA
5. & 6. Implement in GCM, evaluation